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***PETROLOGIA DO COMPLEXO MORRO REDONDO,
PROVÍNCIA GRACIOSA E IMPLICAÇÕES PARA O
MAGMATISMO DE TIPO-A PÓS-COLISIONAL AO
FINAL DO CICLO BRASILIANO – PAN-AFRICANO NO
SUL-SUDESTE DO BRASIL***

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RESUMO

O Complexo Morro Redondo é uma das ocorrências mais importantes e interessantes de granitos de tipo-A e rochas vulcânicas bimodais contemporâneas na Província Graciosa de granitos e sienitos de tipo-A, na região sul do Brasil. As rochas graníticas que compõem o complexo afloram como dois plútons distintos, denominados Papanduva e Quiriri. O Plúton Papanduva inclui álcali-feldspato granitos peralcalinos agrupados em fácies petrográficas distintas, que incluem variedades maciças, micrograníticas e com texturas deformacionais tardi- a pós-magmáticas protomiloníticas e cataclásticas. Anfibólios e clinopiroxênios são os máficos principais. Incluem ferrichterita, arfvedsonita e egirina tardi-magmáticas e egirina-augita e riebeckita pós-magmáticas. Suas principais variações composicionais estão relacionadas com aumento de Na e Fe^{3+} concomitante à diminuição de Ca, Fe^{2+} e Ti do núcleo para as bordas dos cristais, enquanto as abundâncias de elementos-traços sofrem forte influência da composição dos líquidos residuais em equilíbrio, tipicamente enriquecidos em álcalis, elementos HFS, ETR e F, com a circulação sendo favorecida por eventos deformacionais tardios, que também contribuem para a elevação das razões $\delta^{18}\text{O}$ em diversos minerais. Esses líquidos e fluidos evoluem para condições progressivamente mais oxidantes, até temperaturas tão baixas quanto 426 °C nos estágios pós-magmáticos. Essa evolução é acompanhada pela precipitação concomitante de uma diversidade de minerais acessórios de ocorrência rara, tipicamente ricos em elementos HFS e ETR, tais como nacareniobsita, britholita e turkestanita. Por sua vez, o Plúton Quiriri é formado principalmente por biotita sieno- e monzogranitos maciços, de composição levemente peraluminosa. A biotita mostra razões $\text{Fe}^t/(\text{Fe}^t+\text{Mg})$ entre 0,56 e 0,70 com correlações positivas entre F e Fe. Em ambos os plútons, os granitos são caracterizados por composições ricas em Fe (granitos *ferroan*), álcalis e elementos HFS. Os tipos mais evoluídos, tipicamente do Plúton Papanduva, são granitos HHP, com produção de calor radiogênico de até $5,7 \mu\text{Wm}^{-3}$. Datações U-Pb em zircão por LA-ICP-MS revelam que os plútons se colocaram entre 580 Ma e 584 Ma, durante estágios pós-colisionais subsequentes à amalgamação do Supercontinente Gondwana, ao final do Ciclo Brasileiro/Pan-Africano.

Estimativas geotermobarométricas apontam para colocação magmática sob baixas P (≈ 1 kbar), em temperaturas de até 850 – 800 °C e condições relativamente reduzidas (QFM) e oxidantes ($+1 < \Delta_{\text{QFM}} < +3$) para os Plútons Papanduva e Quiriri, respectivamente. A geração dos magmas graníticos do Complexo Morro Redondo parece envolver áreas-fontes de composição isotopicamente evoluída, possivelmente no manto, como apontam as assinaturas tipicamente mantélicas de $\delta^{18}\text{O}/^{16}\text{O}$ em zircão (ca. 4,8 – 6,0 ‰). Os valores de $\varepsilon_{\text{Nd}}(t)$ (ca. -16 a -27) e $\varepsilon_{\text{Hf}}(t)$ ($t = 580\text{Ma}$) (-15 a -35) são fortemente negativos e contrastantes, com o Plúton Quiriri se mostrando menos radiogênico. As idades T_{DM} são equivalentes, variando principalmente entre 2,5 e 3,0 Ga, sugerindo que a colocação e cristalização foi acompanhada de contaminação em graus variáveis por rochas crustais Paleoproterozoicas do embasamento da Microplaca Luiz Alves.

ABSTRACT

The Morro Redondo Complex is one of the most important and interesting occurrences of A-type granites and associated bimodal volcanic rocks from the Graciosa A-type Province, in south Brazil. Granitic rocks that build up the complex crop out as two distinct plutons, namely Papanduva and Quiriri. The Papanduva Pluton includes peralkaline alkali-feldspar granites grouped into contrasting petrographic facies that include massive, microgranitic and deformed (protomylonitic and cataclastic) varieties. Na-Ca- and Na-amphiboles and clinopyroxenes are the main mafic minerals. They include late-magmatic ferrichterite, arfvedsonite and aegirine, and post-magmatic aegirine-augite and riebeckite. The main compositional trends are related to increasing Na and Fe^{3+} and decreasing Ca, Fe^{2+} and Ti contents from core to crystal rims, while the trace-element abundances are strongly influenced by the composition of liquids in equilibrium, typically alkali-, HFSE-, REE- and F-rich, with the circulation being favored by late deformational events that also have contributed to the $\delta^{18}\text{O}$ elevation in many minerals. These liquids and fluids evolved through progressively more oxidizing conditions, at temperatures as low as 426 °C during post-magmatic stages. Liquid evolution is followed by concomitant precipitation of rare, HFSE- and REE-bearing accessory minerals, such as nacareniobsite, britholite and turkestanite. The Quiriri Pluton, on the other hand, is made mainly of massive, slightly peraluminous biotite sieno- and monzogranites. Biotite registers $\text{Fe}^{\text{I}}/(\text{Fe}^{\text{I}}+\text{Mg})$ ratios between 0.56 and 0.70 with positive correlations between F and Fe. In both plutons, granites are characterized by Fe- (ferroan), alkali- and HFSE-rich compositions. The most evolved types, typically from the Papanduva Pluton, are HHP granites, with radiogenic heat production up to $5.7 \mu\text{Wm}^{-3}$. LA-ICP-MS U-Pb dating on zircon reveal that these plutons were emplaced between 580 and 584 Ma, during post-collisional stages that followed the amalgamation of the Gondwana Supercontinent, at the end of the Brasiliano/Pan-African Cycle. Geothermobarometric estimates point to magmatic emplacement under low P (≈ 1 kbar) at temperatures up to 850 – 800 °C and relatively reduced (QFM) and oxidized ($+1 < \Delta_{\text{QFM}} < +3$) conditions for the Papanduva and Quiriri Plutons, respectively. The generation of the granitic

magmas of the Morro Redondo Complex seems to involve isotopically evolved source-areas, probably in the mantle, as indicated by the $\delta^{18}\text{O}/^{16}\text{O}$ zircon mantelic signatures (ca. 4,8 – 6,0 ‰). The $\epsilon\text{Nd}(t)$ (ca. -15 to -27) and $\epsilon\text{Hf}(t)$ ($t = 580\text{Ma}$) (ca. -15 to -35) values are strongly negative and contrasting, with the Quiriri Pluton always as the less radiogenic. T_{DM} ages are equivalent for both plutons, ranging mainly between 2.5 and 3.0 Ga, suggesting that the emplacement and crystallization was followed by contamination in various degrees with Paleoproterozoic crustal components from the basement of the Luiz Alves Microplate.

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PARTE I

INTRODUÇÃO

I. APRESENTAÇÃO E ESTRUTURAÇÃO DA TESE

Esta Tese apresenta um estudo integrado e multimetodológico de rochas graníticas de tipo-A que compõem o Complexo Morro Redondo, no contexto da Província Graciosa de granitos e sienitos de tipo-A, formada em ambientes extensionais ao final do ciclo Brasileiro/Pan-Africano (ca. 580 – 583 Ma) na região sul-sudeste do Brasil.

A Tese está organizada em cinco partes principais. A parte I contempla uma breve introdução à problemática abordada, apresentação da área de estudo e os principais objetivos alcançados. Na parte II encontram-se descritos em algum detalhe os materiais e métodos empregados para a concretização dos objetivos pretendidos. A parte III reúne algumas discussões e considerações finais sobre potenciais áreas-fonte para os magmas que construíram o Complexo Morro Redondo; dados e discussões adiantados nesta parte, com destaque para as informações isotópicas, serão objeto de integração geral com as publicações em andamento para um trabalho a ser submetido brevemente. A parte IV traz, na forma de anexos, quatro manuscritos que se encontram submetidos em periódicos especializados, aos quais se adiciona mais um, já publicado. Por fim, na parte V são reunidos, na forma de tabelas, todos os resultados analíticos obtidos durante este trabalho e que consubstanciam as interpretações alcançadas.

II. PROBLEMÁTICA E ÁREA DE ESTUDO

Dentre todas as camadas que constituem o Planeta Terra, a crosta continental, em especial sua porção superior, é sem dúvida a parte mais acessível aos geocientistas empenhados em desvendar os processos que deram origem ao nosso planeta. Uma característica importante da

crosta continental é o fato dela ser formada por materiais compostos essencialmente por quartzo e feldspatos, com baixa densidade relativa e que dificilmente entram em subducção. Tal característica, além de diferenciá-la da crosta oceânica passível de reciclagem por processos de subducção, torna a crosta continental um dos principais registros de como as condições na Terra mudaram e de como os processos de geração crustal evoluíram ao longo do tempo geológico (Kemp & Hawkesworth, 2004).

As rochas graníticas, seus equivalentes vulcânicos, bem como rochas metamórficas originadas a partir de protolitos graníticos e mesmo rochas sedimentares formadas de clastos cuja origem é granítica são os componentes mais abundantes da crosta continental superior (e.g. Wedepohl, 1991; Pitcher, 1993; Barbarin, 2011), fornecendo assim importantes informações sobre suas propriedades reológicas e evolução composicional. A relativa simplicidade mineralógica dos granitos (compostos basicamente de quartzo e feldspatos) mascara, contudo, sua natureza extremamente complexa, como já era observado desde o Século XVIII pelo naturalista francês Georges Louis Leclerc, Conde de Buffon, que escreveu “*o granito é a rocha mais simples e a mais variada: a mais simples uma vez que consiste apenas de quartzo e feldspato, e a mais variada por causa dos tipos mineralógicos e ambientes geodinâmicos associados*”. Na realidade, cada corpo granítico é a representação de uma história evolutiva distinta e multifacetada. Como aponta Eiler (2007), muitos são compostos de minerais cristalizados diretamente de fusões magmáticas; alguns representam combinações de minerais cristalizados a partir de diferentes magmas e posteriormente misturados durante longos episódios da evolução e resfriamento das câmaras magmáticas e outros ainda podem conter frações remanescentes das áreas-fontes ou ainda xenólitos capturados das rochas encaixantes e dos condutos. De fato, os minerais formadores de granitos não raramente apresentam composições químicas e isotópicas heterogêneas, refletindo processos evolutivos complexos de seus magmas parentais durante o curso de cristalização, incluindo frequentes eventos de contaminação por rochas encaixantes (e.g. White, 1979; Clarke, 1992; Pitcher, 1993; Barbarin, 1999; Winter, 2001). Neste panorama, parece claro que as rochas graníticas são excelentes fontes de informação sobre a diversidade de possíveis áreas-fontes

mantélicas ou da crosta inferior, além de distintas condições de formação, processos evolutivos e de colocação.

A variabilidade textural, mineralógica e composicional das rochas graníticas tem sido extensivamente abordada em sistemas classificatórios a partir da década de 70, que passaram a utilizar implicações genéticas para individualizar grupos de granitos. Assim, o célebre manuscrito de Chapell & White (1974) introduziu a definição de granitos de tipo-I, derivados de rochas ígneas infracrustais e tipo-S, interpretados como resultado da anatexia de protolitos sedimentares (ver também White & Chapell, 1983; Eiler, 2007; Kemp et al., 2007). Seguindo nesta linha, Loiselle & Wones (1979) definiram um grupo específico de granitos (e rochas félsicas associadas) denominados de “tipo-A”, de natureza anorogênica, com tendência alcalina e formado sob baixas fugacidades de H_2O e O_2 . Este trabalho, apresentado na forma de resumo simples numa reunião da *Geological Society of America*, não foi procedido de nenhum estudo mais aprofundado por parte de seus autores, fato que contribuiu significativamente para a confusão criada em torno de alguns atributos de magmas félsicos de tipo-A (ver revisão em Bonin, 2007; Frost & Frost, 2011), uma vez que coube a outros pesquisadores desenvolver as bases teóricas e modelos para esse novo grupo de granitos. Isso por outro lado trouxe enorme avanço para a sua caracterização geoquímica, isotópica e de condições de P-T e fO_2 de formação (e.g. Whalen, 2005).

Os granitos de tipo-A incluem diversas associações petrográficas com afinidades geoquímicas e isotópicas contrastadas (álcali-cálcicas, “subalcalinas” a alcalinas, metaluminosas, peralcalinas ou ainda marginalmente peraluminosas, com razões Fe/Mg altas a muito altas; e.g. Whalen et al., 1987; Vlach et al., 1990; Eby, 1992; King et al., 1997; Frost et al., 2001, Gualda & Vlach, 2007a; Frost & Frost, 2011). São rochas enriquecidas em álcalis, elementos de alto potencial iônico (HFS), especialmente Zr, Nb e Y e elementos terras-raras (ETR), e empobrecidas em Ca, Ba, Sr, e Eu (cf. por exemplo, Whalen et al., 1987; King et al., 2001; Bonin, 2007). São formadas sob condições *redox* ora mais oxidantes, ora mais redutoras (e.g. Anderson & Bender, 1989; Dall’Agnol et al., 1999; Dall’Agnol & Oliveira, 2007), não somente em ambientes anorogênicos continentais ou oceânicos, mas também pós-orogênicos e/ou pós-colisionais, em regimes tectônicos extensionais na crosta continental. Em geral, as intrusões são notadamente rasas ou

mesmo subvulcânicas, onde podem formar complexos anelares e plútons circunscritos ou mais irregulares, com frequência associados com vulcanismo bimodal, em que predominam amplamente termos básicos e ácidos.

Províncias magmáticas de tipo-A ocorrem em um intervalo de aproximadamente 3 bilhões de anos da história geológica da Terra, desde ca. 2,7 Ga até o presente e a elas encontram-se associadas diversas mineralizações de grande importância econômica, tais como Sn, F, Nb, Ta, Au, Fe, U, elementos terras-raras (ETR) (Whalen et al., 1987; Eby, 1990; Dall'Agnol et al., 1999; 2005; Bonin, 2005; 2007; Heinonen et al., 2010). Merece também ser destacado que esse grupo de granitos é ainda, senão o único presente, pelo menos melhor representado em outros planetas rochosos (Vênus e Marte, além da Lua) e no cinturão de asteroides (cf. Bonin, 2007 e referências citadas).

Os granitos de tipo-A são essenciais para a compreensão dos processos magmáticos associados a ambientes extensionais intraplaca e pós-orogênicos/colisionais (e.g. Martin, 2006), bem como contribuem para a construção da crosta continental superior, em especial para o seu enriquecimento em elementos HFS relativamente ao TiO_2 (Turner et al., 1992; Kemp & Hawkesworth, 2004). Paralelamente, o relativo enriquecimento em elementos radioativos como Th e U contribuem para significativo aumento dos valores médios da produção de calor radiogênico nas zonas mais rasas da crosta continental (e.g., Jaupart & Mareschal, 1999; 2010).

A grande variabilidade de litotipos agrupados sob o rótulo “tipo-A” aponta para a existência de “granitos e granitos” de tipo-A (Bonin 2007), e ainda não há um consenso geral sobre os principais modelos petrogenéticos envolvidos na sua gênese. Assim, algumas questões fundamentais relacionadas ao envolvimento de diferentes reservatórios-fonte do manto, bem como as contribuições de diferentes segmentos da crosta continental, ainda carecem de exploração científica. Estes, entre outros fatos levaram recentemente, por exemplo, a que Frost & Frost (2011) sugerissem que o termo fosse descontinuado e substituído por “granitos ferroanos”, um neologismo para o termo “*ferroan granites*” dos referidos autores (ver também Heinonen et al., 2010).

A ocorrência de granitos de tipo-A de natureza metaluminosa a peralcalina (*associação alcalina*; Lameyre & Bowden, 1982) e metaluminosa a moderadamente peraluminosa (*associação*

aluminosa; Vlach et al., 1990, King et al., 1997) em uma mesma província pós-colisional permite examinar os diversos mecanismos que resultam em tal diversidade, além de permitir a coleta de dados que ajudem a identificar modelos petrogenéticos e áreas-fontes envolvidas. Na região sudeste do Brasil, a Província Graciosa de granitos e sienitos de tipo-A (Gualda & Vlach, 2007a) contempla estes quesitos. Nos últimos anos, esta província tem sido alvo de diversos estudos petrográficos, mineralógicos, geoquímicos, isotópicos e geocronológicos (e.g. Garin et al., 2003; Gualda & Vlach, 2007a; 2007b; 2007c; Vlach & Gualda, 2007; Vilalva, 2004; 2007; Vilalva & Vlach, 2010; Koch, 2010; Vogado, 2010; Garcia, 2011; Vlach et al., 2011), trazendo luz ao melhor entendimento do magmatismo de “tipo-A” associado, neste contexto, a regimes tectônicos extensionais durante estágios pós-colisionais ao final do Ciclo Orogênico Brasileiro/Pan-Africano.

Dentre os diversos plútons que compõem a Província Graciosa, o Complexo Morro Redondo (Góis, 1995) é uma das ocorrências mais importantes e interessantes. Localizado entre as cidades de Tijucas do Sul (PR) e Garuva (SC), às margens da rodovia BR-376 (Fig. 1), é formado pelos Plútons Papanduva e Quiriri, em que afloram rochas graníticas de tipo-A das associações alcalina e aluminosa, respectivamente. Em particular, os granitos do Plúton Papanduva, de natureza peralcalina, estão entre os tipos peralcalinos mais evoluídos da Província Graciosa, alguns deles portando fases minerais raras, diversas entre elas descritas pela primeira vez em rochas graníticas do Brasil, em arranjos texturais tardi - a pós-magmáticos de especial interesse (e.g. Vilalva & Vlach, 2006; Vlach & Vilalva, 2007; Vilalva & Vlach, 2010). Além disso, o complexo é um das poucas ocorrências da província onde se pode reconhecer um vulcanismo bimodal contemporâneo, cujos termos ácidos (comenditos e pantelleritos) compartilham as características geoquímicas com os granitos do Plúton Papanduva. A conjunção desses fatores motivou em 2004 o início de investigações mineralógicas e petrológicas sistemáticas mais aprofundadas para o complexo, uma vez que até aquele momento se dispunha de uma quantidade relativamente restrita de dados de tipo petrográfico, mineralógico, geoquímico e isotópico, considerando-se as dimensões da ocorrência (~250 Km²). Adicionalmente, os dados disponíveis (e.g. Machado et al., 1993; Siga Jr et al., 1994; 1997; Góis, 1995; Kaul, 1997; Kaul & Cordani, 2000; Valley et al., 2005) geralmente não foram obtidos de forma sistemática. Os resultados

parciais obtidos culminaram na elaboração de uma Monografia de Trabalho de Formatura (Vilalva, 2004) e de uma Dissertação de Mestrado (Vilalva, 2007), além de contribuições científicas diversas na forma de um artigo completo (Vilalva & Vlach, 2010) e resumos expandidos e simples (e.g. Vilalva & Vlach, 2006a; 2006b; Vilalva & Vlach, 2007; Vlach & Vilalva, 2007; Vilalva & Vlach, 2009; Vilalva & Vlach, 2010).

Neste panorama, a presente Tese de Doutorado representa o detalhamento dos estudos no Complexo Morro Redondo, trazendo novos dados que permitem embasar melhor a compreensão da petrogênese e da evolução deste magmatismo granítico.

II.1. CONTEXTUALIZAÇÃO GEOLÓGICA DA ÁREA DE ESTUDO

O Complexo Morro Redondo está situado na porção sul da Província Graciosa, estendendo-se por cerca de 25 Km, com largura entre 10 e 13 km e cobrindo uma área de ~250 km². Os Plútons Serra da Igreja, Dona Francisca e Piraí são os componentes da província mais próximos (Fig. 1). O complexo possui uma orientação geral segundo N20°W, disposto paralelamente à Zona de Cisalhamento Rio Palmital-Serrinha que o separa, a leste, dos granitoides cálcio-alcálicos do tipo Estrela do Terreno Paraguá (e.g. Siga Jr et al., 1993; 1994).

A Província Graciosa agrupa granitos e sienitos de tipo-A que afloram como plútons alongados ou levemente circulares na porção centro-sul da Província Estrutural Mantiqueira, desde o extremo sudeste de São Paulo, nas proximidades de Cajati, até o nordeste de Santa Catarina, próximo a Corupá. Os plútons são intrusivos em rochas Arqueanas da Microplaca (Cráton) Luiz Alves e em rochas Paleo- a Neoproterozoicas da Microplaca Curitiba e do Terreno Paraguá (e.g. Siga Jr. et al., 1993; Vlach & Gualda, 2007a; Basei et al., 2008; Fig. 1), e se encontram associados com bacias vulcanossedimentares contemporâneas (e.g. Bacias de Campo Alegre e Guaratubinha; Siga Jr. et al., 2000).

As rochas graníticas e sieníticas da província exibem estruturas predominantemente maciças, com feições texturais indicativas de colocação em níveis crustais rasos (ca. 2 kbar,

Gualda & Vlach, 2007a) e são agrupadas em duas associações petrográficas de características texturais e químicas contrastantes: 1) *Associação Alcalina*, composta de álcali-feldspato granitos e álcali-feldspato sienitos hipersolvus, leucocráticos, de caráter metaluminoso a peralcalino; e 2) *Associação Aluminosa*, caracterizada por granitos e álcali-feldspato granitos de caráter metaluminoso a moderadamente peraluminoso. O quadro litológico da província se completa com diversas ocorrências de rochas gabro-dioríticas e monzodioríticas, bem como rochas vulcânicas básicas a ácidas associadas a diversos plútons (e.g. Plútons Órgãos e Corupá, Complexo Morro Redondo; Fig. 1). Datações U-Pb em zircão de alguns desses dioritos indicam idades de cristalização Neoproterozoicas, entre 580 – 583 Ma, interpretadas como a melhor idade de referência para a província (Vlach et al., 2011).

O magmatismo neoproterozoico de tipo-A formador da Província Graciosa tem sua origem associada a regimes tectônicos extensionais posteriores a aglutinação final dos diversos blocos e terrenos crustais que resultaram na formação do Supercontinente Gondwana na região sul-sudeste do Brasil (e.g. Basei et al., 1992; Siga Jr. et al., 1993).

Figura 1: Mapa geológico esquemático das principais unidades geológicas do sul-sudeste brasileiro: 1 - Coberturas Fanerozóicas; 2 - Complexos alcalinos mesozoicos; 3 - Bacia Eopaleozóica; 4 - Bacias Neoproterozóicas; [Neoproterozoico] 5 - Stocks graníticos de características de tipo-A do Domínio Apiaí; **6 - Granitos e sienitos de tipo-A da Província Graciosa**; 7 - Vulcânicas ácidas e básicas; 8 - Batólito Três Córregos; 9 - Batólito cálcio-alcalino Piên-Mandirituba; 10 - Batólito Paranaguá; **DOMÍNIO APIAÍ:** 11 - Formação Iporanga; 12 - Grupo Itaiacoca; 13 - Subgrupo Lageado; [Mesoproterozoico] 14 - Formação Águas Claras; 15 - Formação Votuverava; [Paleoproterozoico] 16 - Formação Perau; 17 - Núcleos granito-gnáissicos alcalinos (tipo-A); **MICROPLACA CURITIBA:** [Neoproterozoico] 18 - Formação Capiuri; 19 - Sequência Turvo-Cajati; [Paleoproterozoico] 20 - Complexo Atuba; **MICROPLACA LUÍS ALVES:** [Arqueano-Paleoproterozoico] 21 - Complexo Granulítico de Santa Catarina; **TERRENO PARANAGUÁ:** [Neoproterozoico] 22 - Metassedimentos protomiloníticos (Sequência Rio das Cobras); 23 - Zonas de cisalhamento (ZCI: Zona de Cisalhamento Itapirapuã; ZCMA: Morro Agudo; ZCR: Ribeira; ZCLC: Lancinha-Cubatão; ZCMP: Mandirituba-Piraquara; ZCRPSR: Rio Palmital-Serrinha; ZCPT: Piên-Tijucas. Adaptado e modificado de Prazeres Filho et al., 2003, Heilbron et al., 2004 e Gualda & Vlach, 2007a).

III. OBJETIVOS E APRESENTAÇÃO DOS RESULTADOS

Modelos evolutivos e interpretações petrogenéticas para um corpo ígneo dependem fundamentalmente da aquisição e interpretação de dados geológicos, petrográficos, mineralógicos e geoquímicos sólidos e consistentes que possam ser adequadamente integrados. Os trabalhos citados no item anterior forneceram um sólido e extenso acervo de dados mineralógicos (texturais e químicos) e petrográficos para o Complexo Morro Redondo, com ampla ênfase para o Plúton Papanduva. O presente trabalho teve como objetivo central o aprofundamento do nível de conhecimento do Complexo Morro Redondo em quatro frentes principais inter-relacionadas:

- a) Estudos petrográficos e mineralógicos de detalhe,
- b) Determinações geocronológicas U-Pb em zircão por LA-ICP-MS,
- c) Investigações geoquímicas (EPMA e LA-ICP-MS) e isotópicas (isótopos de Hf e O) em minerais,
- d) Investigações geoquímicas (ICP-MS e FRX) e isotópicas (Rb-Sr e Sm-Nd, TIMS) em rocha-total.

Partindo dessas estratégias, os objetivos específicos alcançados são colocados a seguir. À exceção das investigações isotópicas em rocha-total e Lu-Hf em zircão que são discutidas brevemente na Parte III e deverão ser incluídas em trabalho futuro, os demais resultados são apresentados na forma de artigos completos submetidos a periódicos especializados, conforme Parte IV da Tese. São eles:

- i. **Anexo A:** manuscrito submetido aos Anais da Academia Brasileira de Ciências: “*Geology, petrography and geochemistry of the A-type granites from the The Morro Redondo Complex (PR-SC), South Brazil, Graciosa Province*” (Vilalva, F.C.J. & Vlach, S.R.F.). Apresenta e discute os dados geológicos, petrográficos e mineralógicos de detalhe (incluindo análises química via EPMA para biotita e feldspatos) e de suscetibilidade magnética (SM) obtidos para o Plúton Quiriri e complementados para o Plúton Papanduva, bem como os dados de

química de rocha-total (elementos maiores, menores e traços) obtidos para ambos os plútons.

- ii. **Anexo B:** manuscrito submetido à revista *Precambrian Research*, sob o título: “*In-situ U-Pb dating and trace element compositions of zircon from the Graciosa A-type Province, South Brazil: insights for the timing of extensional magmatism at end of the Brasiliano-Pan-African Orogeny*” (Vilalva, F.C.J.; Simonetti, A.; Vlach, S.R.F.), que discute determinações geocronológicas U-Pb e composição de elementos traços obtidos em cristais de zircão com LA-ICP-MS obtidos para os Plútons Papanduva e Quiriri, e de riolito contemporâneo do Complexo Morro Redondo, bem como de outras ocorrências-chave de granitos e sienitos da Província Graciosa, objetivando o detalhamento das idades de colocação dos constituintes principais da província.
- iii. **Anexo C:** manuscrito submetido à *Lithos* “*Chemical evolution (major and trace elements) and oxygen isotope ratios of amphiboles and clinopyroxenes from A-type granites of the papanduva pluton, graciosa province, S Brazil: insights into the late- to post-magmatic evolution of peralkaline melts and fluids*” (Vilalva, F.C.J.; Vlach, S.R.F.; Simonetti, A.). Apresenta e discute composições de elementos traços (LA-ICP-MS) e isótopos estáveis de O para anfibólios e piroxênios do Plúton Papanduva, complementados com os dados de química de elementos maiores e menores obtidos via microsonda eletrônica por Vilalva (2007), com inferências relevantes para a evolução tardi- a pós-magmática do Plúton Papanduva.
- iv. **Anexo D:** manuscrito submetido à revista *Canadian Mineralogist* intitulado “*Nacarebiosite-(Ce) and britholite-(Ce) in peralkaline granites from the Morro Redondo Complex, Graciosa Province, Southern Brazil: occurrence and compositional (EPMA, LA-ICP-MS) data*” (Vilalva, F.C.J.; Vlach, S.R.F.; Simonetti, A.). Este manuscrito apresenta dados inéditos de elementos traços (LA-ICP-MS) obtidos em cristais de nacareniobsita e britholita, minerais acessórios raros tardi- a pós-magmáticos encontrados nas variedades mais evoluídas do Plúton Papanduva. Os resultados são complementados com os dados de EPMA

apresentados em Vilalva (2007) e interpretados à luz de informações existentes em literatura. Representa uma contribuição à mineralogia do Pluton Papanduva e de rochas graníticas peralcalinas de forma geral e a sua evolução tardi-magmática.

- v. **Anexo E:** Manuscrito publicado na revista *Mineralogical Magazine*, vol 74(4) de 2010, pp. 645–658: “*Major- and trace-element composition of REE-rich turkestanite from peralkaline granites of the Morro Redondo Complex, Graciosa Province, south Brazil*” (Vilalva, F.C.J. & Vlach, S.R.F.). Apresenta e discute composição química de elementos maiores (dados EPMA de Vilalva, 2007) e traços obtidos via LA-ICP-MS em cristais de turkestanita, outro raro mineral acessório identificado no Plúton Papanduva, com importantes implicações para a evolução tardi- a pós-magmática dos líquidos e fluidos peralcalinos das rochas graníticas.

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PARTE II

MATERIAIS E MÉTODOS

A investigação moderna de processos genéticos, evolutivos e modificadores de magmas graníticos possui como alicerce uma abordagem multidisciplinária cuja sequência de métodos é em geral bem estabelecida e inclui mapeamento geológico e faciológico, análises petrográficas, mineralógicas e geoquímicas e isotópicas em minerais e em rocha-total, incluindo técnicas geocronológicas. Este trabalho segue essa tendência e uma discussão pormenorizada e sequencial dos métodos e abordagens utilizados é apresentada a seguir.

I. TRABALHOS DE CAMPO

As atividades de campo específicas deste trabalho foram desenvolvidas ao longo de três anos empregando-se para tal, técnicas clássicas de mapeamento e coleta de amostras, em especial a sistemática de mapeamento faciológico discutida em Ulbrich et al. (2001; ver também Vlach, 1993).

O mapeamento faciológico e estudos petrográficos e mineralógicos detalhados para o Plúton Papanduva foram apresentados e discutidos por Vilalva (2007), razão pela qual se dispõe de uma boa amostragem das principais unidades de mapeamento individualizadas. Desta forma, os trabalhos de campo deste trabalho foram focalizados no Plúton Quiriri, cujo nível do conhecimento geológico, bem como a amostragem disponível, situavam-se até aquele momento, em um grau bastante insatisfatório. Os trabalhos consistiram de reconhecimento, descrição e mapeamento das principais fácies petrográficas, procura de possíveis relações de contato com o Plúton Papanduva, bem como coleta sistemática de amostras representativas para estudos petrográficos, mineralógicos, geoquímicos e isotópicos de maior detalhe. Esta última atividade nem sempre se mostrou de fácil concretização, tendo em vista a dificuldade de se obter amostras frescas e em

dimensões adequadas em uma região de proteção ambiental, caracterizada por relevos muito acidentados, clima úmido e densas coberturas vegetais da Mata Atlântica.

As etapas de campo foram efetuadas durante cerca de 45 dias, nos quais foram visitados e descritos 120 afloramentos, com coleta de cerca de 150 amostras representativas para estudos em laboratório. As cartas topográficas SG.22-X-D-V-3 (Pedra Branca do Araraquara), SG.22-Z-B-II-1 (Garuva), SG.22-X-D-IV-4 (Tijucas do Sul) e SG.22-Z-B-I-2 (São Miguel), imagens de satélite do sistema Landsat-7 ETM+ (bandas 3, 4, 5, com resolução de 30 m; e pancromática, com resolução de 15 m) correspondente à cena 220-078 (data de passagem 07/05/2000), equipamento de posicionamento global portátil Garmin GPSMap 76 CsX e suscetibilímetro magnético de bolso foram utilizados como suporte para os trabalhos de campo.

II. ANÁLISES PETROGRÁFICAS

Análises petrográficas foram realizadas em cerca de 30 seções delgadas convencionais e delgadas-polidas em microscópio Zeiss, modelo Axioplan-pol, sob luzes transmitida e refletida no Laboratório de Ótica do Instituto de Geociências da Universidade de São Paulo, SP (IGc-USP), seguindo técnicas e abordagens clássicas de microscopia petrográfica, como aquelas descritas em Williams et al. (1982) e Hibbard (1995; ver também McKenzie et al., 1995). Os trabalhos de Tröger (1979), Deer et al. (1992) e Pracejus (2008) foram utilizados como guias para a identificação dos minerais acessórios presentes de reconhecimento mais difícil. As análises incluíram o reconhecimento e caracterização das principais fases minerais e acessórios e suas relações texturais, tendo em vista estabelecer possíveis paragêneses e sequências de cristalização, bem como procurar distinguir através das texturas observadas, eventos magmáticos, tardi- e pós-magmáticos de cristalização, tarefa esta que se mostrou nada expedita em diversos casos. A identificação e definição de microestruturas e texturas relacionadas com eventos deformacionais tardi- a pós-magmáticos recebeu também atenção especial (e.g. Vernon, 2004).

O registro fotográfico macro- e microscópico das texturas e fases minerais principais, acessórias e ocasionais foi efetuado com o emprego, respectivamente, das câmeras fotográficas digitais Olympus Stylus 740 de 7,1 megapixels de resolução máxima e 5x de zoom ótico máximo e Olympus C5050Z, com resolução máxima de 5,0 megapixels e 5x de zoom ótico máximo, acoplada ao microscópio Olympus modelo BXP-50, do Laboratório de Ótica do IGc-USP.

Durante os estudos petrográficos procedeu-se também à seleção de cristais representativos de cada geração textural das fases minerais principais e acessórias mais típicas para análises químicas pontuais em microsonda eletrônica e LA-ICP-MS.

III. DETERMINAÇÕES DE SUSCETIBILIDADES MAGNÉTICAS

Medidas de suscetibilidade magnética (SM) foram efetuadas com o suscetibilímetro portátil da GF Instruments, modelo SM 20, tomando-se em torno de 10 medidas por amostra. As medições foram efetuadas no campo, em superfícies frescas e o mais plano possível e também em laboratório, sobre fatias de rocha, de forma a complementar o banco de dados disponibilizado em Vilalva (2007). O tratamento foi feito no programa Systat 12.02, em plataforma Windows. Consideraram-se as médias de 10 determinações, eliminando eventuais medidas que se distanciaram por demais da média e moda, de acordo com os desvios padrões calculados.

IV. ANÁLISES GEOQUÍMICAS EM MINERAIS

IV.1. ANÁLISES COM MICROSSONDA ELETRÔNICA (EPMA)

Um extenso acervo de dados de quimismo mineral *in situ* para minerais félsicos, máficos e acessórios principais do Plúton Papanduva foi apresentado por Vilalva (2007). Para o Plúton Quiriri uma pequena coleção de dados que permitiram uma caracterização química mais geral de feldspatos, hornblenda e biotita é apresentada por Vilalva (2004). Desta forma, para o presente

trabalho foram efetuadas apenas análises WDS complementares em cristais de feldspato alcalino, plagioclásio e biotita do Plúton Quiriri, selecionados segundo critérios texturais mais rigorosos em seções delgado-polidas cobertas com uma película de C de *ca.* 25 nm, com evaporador modelo Auto 306 da Edwards.

O equipamento utilizado foi a microsonda eletrônica JEOL modelo JXA-8600S do Laboratório de Microsonda Eletrônica do GMG-IGc/USP. O equipamento conta com detector ED e cinco espectrômetros WD, cada qual com dois cristais analisadores (STE/TAP, TAP/PET, PET/LiF, PET/LiF, PET/LiF), e sistema de automação Voyager 4.4 da Thermo-Noran. Imagens de elétrons retro-espalhados em modo composicional (BSE-Compo) foram obtidas para a verificação de possíveis zonamentos químicos não detectados ao microscópio ótico, bem como para otimizar a localização dos melhores pontos analíticos em zonas cristalinas de interesse. As condições analíticas empregadas foram de 15 kV, 20 nA e 1 μ m, respectivamente para a voltagem de aceleração, corrente e diâmetro do feixe eletrônico focado na superfície da seção delgado-polida.

As análises químicas quantitativas WDS foram efetuadas sob 15 kV, 20 nA e 5 μ m, respectivamente para a voltagem de aceleração, corrente e diâmetro do feixe eletrônico. Para os feldspatos alcalinos, o diâmetro do feixe foi igual a 5 μ m para pertitas e mesopertitas com lamelas de exsolução bem desenvolvidas, e 20 μ m para as pertitas e mesopertitas com lamelas mais finas, para os quais este diâmetro permitiria uma integração adequada das intensidades. Cerca de 20 seções delgado-polidas representativas foram selecionadas. Em cada uma, entre 3 e 5 cristais de cada geração textural de biotita, feldspato alcalino e plagioclásio foram analisados. Os elementos analisados, linhas espectrais usadas para quantificação, cristais analisadores, padrões e tempos totais de integração de contagens utilizados para cada mineral são apresentados na Tabela 1. As correções dos efeitos de matriz (número e absorção atômicos, fluorescência secundária) e redução dos valores de intensidades para porcentagens em peso de elementos e/ou óxidos foram efetuadas utilizando o programa PROZA (Bastin & Heijligers, 1990), disponível no sistema de automação da Thermo-Noran. De um modo geral, a precisão analítica estimada é superior a 2 % relativo para os elementos maiores, entre 5-10 % para os elementos menores e inferior para os elementos traços.

Alguns cristais de feldspato alcalino apresentaram-se com lamelas de exsolução bem desenvolvidas, o que permitiu análises químicas pontuais das fases exsolvidas, bem como do feldspato potássico hospedeiro. Para uma primeira estimativa das composições originais desses feldspatos foi feita a integração de imagens de elétrons retro-espalhados com os dados químicos pontuais, com feixe eletrônico de 5 µm, obtidos para as fases exsolvidas (albita) e hospedeira (feldspato potássico) em zonas de núcleo, intermediárias e borda de um mesmo cristal, em um procedimento semelhante ao descrito em Gualda (2001) e Vilalva (2007).

A diagramação dos dados para avaliações dos vetores de substituições químicas e análise de tendências evolutivas foi efetuada com o programa Systat SigmaPlot 9.0. As fórmulas minerais e distribuições catiônicas foram calculadas com o programa Mincal (Gualda & Vlach, inédito) considerando-se 22 e 32 átomos de O para biotita e feldspatos, respectivamente.

Tabela 1: Linhas espectrais, cristais analisadores, padrões e tempos de integração de contagens (t) utilizados nas análises WDS de biotita e feldspatos (alcalino e plagioclásio)

linha	cristal	padrões biotita	padrões feldspato	t (s)*
<i>Si Ka</i>	TAP	wollastonita	microclínio	10-20
<i>Ti Ka</i>	LiF	rutilo	rutilo	20-40
<i>Al Ka</i>	TAP	anortita	anortita	10-40
<i>Fe Ka</i>	LiF	Mn-olivina	Mn-olivina	20-30
<i>Mn Ka</i>	LiF	Mn-olivina	Mn-olivina	20-40
<i>Mg Ka</i>	TAP	dipsídio	dipsídio	20-40
<i>Zn Ka</i>	LiF	ZnO	---	20-40
<i>Ca Ka</i>	PET	wollastonita	anortita	10-30
<i>Ba La</i>	LiF	barita	---	30
<i>Na Ka</i>	TAP	albita	albita	10-20
<i>K Ka</i>	PET	microclínio	microclínio	20-40
<i>Cl Ka</i>	PET	apatita	---	10
<i>F Ka</i>	TAP	fluorita	---	10

* Tempo total de integração de contagens igualmente dividido entre pico e radiação de fundo. --- : não analisado.

IV.2. ANÁLISES ELEMENTAIS COM ESPECTROMETRIA DE MASSA EM PLASMA DE INDUÇÃO ACOPLADA (MONO-COLETOR) POR ABLAÇÃO LASER (LA-ICP-MS)

Micro-análises quantitativas de elementos traços para cristais de zircão dos Plútons Papanduva e Quiriri, de outros plútons de interesse da Província Graciosa, bem como para anfibólios, clinopiroxênios e alguns acessórios raros (britholita, nacareniobsita e turkestanita) do Plúton Papanduva foram efetuadas em seções delgado-polidas de 30, 60 e 80 μm com LA-ICP-MS no Laboratório de Química E ICP-AES do IGc-USP e no MITERAC (*Midwest Isotope and Trace Element Research Analytical Center*) da Universidade de Notre Dame, Indiana, EUA, neste caso sob a supervisão do Dr. Antonio Simonetti, no contexto de estágio tipo “sanduíche” (processo Capes BEX 4956/10-9) durante o ano de 2011. Os equipamentos disponíveis nesses laboratórios são, respectivamente: (a) ICP-MS Perkin-Elmer Elan 6100DRC acoplado a um sistema de ablação a laser (*laser ablation*) Y(Nd)AlG de 213 nm da New Wave Research, modelo UP213; (b) ICP-MS de setor magnético ThermoFinnigan Element2 acoplado ao sistema de ablação a laser UP213 da ESI-New Wave. As condições analíticas empregadas para a ablação, os elementos analisados e os padrões internos e externos utilizados são detalhados na Tabela 2. As análises consistiram de 60s para leitura do *background*, seguidas de 60s para aquisição dos dados e ablação, com tempo de integração e *dwell time* de cerca de 1,6 e 8 ms, respectivamente, para cada elemento analisado. A ablação é seguida por 30s de *washout time*. A redução dos dados, correção do *drift* do equipamento, bem como o tratamento e conversão das intensidades em concentrações (ppm) foram efetuadas com o programa Glitter (van Achterbergh et al., 2001). Em alguns casos, em dependência principalmente da susceptibilidade dos minerais analisados, foram efetuadas análises em modo raster (e.g. turkestanita). Para a localização dos pontos e compatibilização com as análises WDS disponíveis, foram utilizadas imagens óticas e BSE, além de imagens de catodoluminescência (CL) e de elétrons secundários (SEI) para as determinações em zircão.

Tabela 2: Condições analíticas do sistema de ablação a laser (LA-ICP-MS) utilizadas para as análises de elementos traços em diferentes minerais

condições	anfíbólios	piroxênios	zircão	britholita	nacarenioobsita	turkestanita
análises individuais (n)	48	37	50	12	6	1
modo de resolução	baixa	baixa	média	baixa	baixa	baixa
diâmetro do laser	40 µm	40 µm	30 µm	40 µm	40 µm	modo raster
duração do pulso	5 ns	5 ns	5 ns	5 ns	5 ns	5 ns
frequência de repetição	2 - 4 Hz	4 Hz	4 Hz	4 Hz	4 Hz	contínuo
energia de saída	75 - 80%	75 - 80%	70%	80 - 85%	80 - 85%	80 - 85%
fluência do laser	15 J/cm ²	15 J/cm ²	10 J/cm ²	15 J/cm ²	15 J/cm ²	15 J/cm ²
padrão externo	NIST-612 BHVO-2G	NIST-612 BHVO-2G	NIST-612 BHVO-2G	NIST-612	NIST-612	NIST-612 BHVO-2G
padrão interno*	Ca	Ca	Si	Ca	Ca	Ca
Elementos analisados	Li ⁷ , Be ⁹ , P ³¹ , Ca ⁴³ , Sc ⁴⁵ , Ti ⁴⁹ , V ⁵¹ , Cr ⁵² , Mn ⁵⁵ , Co ⁵⁹ , Ni ⁶⁰ , Cu ⁶⁵ , Zn ⁶⁶ , Ga ⁷¹ , Rb ⁸⁵ , Sr ⁸⁸ , Y ⁸⁹ , Zr ⁹⁰ , Nb ⁹³ , Mo ⁹⁵ , Sn ¹¹⁸ , Sb ¹²¹ , Cs ¹³³ , Ba ¹³⁷ , La ¹³⁹ , Ce ¹⁴⁰ , Pr ¹⁴¹ , Nd ¹⁴³ , Sm ¹⁴⁷ , Eu ¹⁵¹ , Gd ¹⁵⁵ , Tb ¹⁵⁹ , Dy ¹⁶³ , Ho ¹⁶⁵ , Er ¹⁶⁶ , Tm ¹⁶⁹ , Yb ¹⁷³ , Lu ¹⁷⁵ , Hf ¹⁷⁹ , Ta ¹⁸¹ , Pb ²⁰⁸ , Th ²³² , U ²³⁸	Li ⁷ , Be ⁹ , P ³¹ , Ca ⁴³ , Sc ⁴⁵ , Ti ⁴⁹ , V ⁵¹ , Cr ⁵² , Mn ⁵⁵ , Co ⁵⁹ , Ni ⁶⁰ , Cu ⁶⁵ , Zn ⁶⁶ , Ga ⁷¹ , Rb ⁸⁵ , Sr ⁸⁸ , Y ⁸⁹ , Zr ⁹⁰ , Nb ⁹³ , Mo ⁹⁵ , Sn ¹¹⁸ , Sb ¹²¹ , Cs ¹³³ , Ba ¹³⁷ , La ¹³⁹ , Ce ¹⁴⁰ , Pr ¹⁴¹ , Nd ¹⁴³ , Sm ¹⁴⁷ , Eu ¹⁵¹ , Gd ¹⁵⁵ , Tb ¹⁵⁹ , Dy ¹⁶³ , Ho ¹⁶⁵ , Er ¹⁶⁶ , Tm ¹⁶⁹ , Yb ¹⁷³ , Lu ¹⁷⁵ , Hf ¹⁷⁹ , Ta ¹⁸¹ , Pb ²⁰⁸ , Th ²³² , U ²³⁸	Si ²⁹ , P ³¹ , Sc ⁴⁵ , Ti ⁴⁹ , Mn ⁵⁵ , Sr ⁸⁸ , Y ⁸⁹ , Zr ⁹¹ , Nb ⁹³ , Mo ⁹⁵ , Ba ¹³⁷ , La ¹³⁹ , Ce ¹⁴⁰ , Pr ¹⁴¹ , Nd ¹⁴³ , Sm ¹⁴⁷ , Eu ¹⁵¹ , Gd ¹⁵⁵ , Tb ¹⁵⁹ , Dy ¹⁶³ , Ho ¹⁶⁵ , Er ¹⁶⁶ , Tm ¹⁶⁹ , Yb ¹⁷³ , Lu ¹⁷⁵ , Hf ¹⁷⁹ , Ta ¹⁸¹ , Pb ²⁰⁶ , Pb ²⁰⁸ , Th ²³² , U ²³⁸	Li ⁷ , Be ⁹ , Mg ²⁵ , Ca ⁴³ , Sc ⁴⁵ , Ti ⁴⁹ , V ⁵¹ , Cr ⁵² , Mn ⁵⁵ , Co ⁵⁹ , Ni ⁶⁰ , Cu ⁶⁵ , Ga ⁷¹ , Rb ⁸⁵ , Sr ⁸⁸ , Y ⁸⁹ , Zr ⁹⁰ , Nb ⁹³ , Sn ¹¹⁸ , Cs ¹³³ , Ba ¹³⁷ , Ce ¹⁴⁰ , Pr ¹⁴¹ , Nd ¹⁴³ , Sm ¹⁴⁷ , Eu ¹⁵¹ , Gd ¹⁵⁵ , Tb ¹⁵⁹ , Dy ¹⁶³ , Ho ¹⁶⁵ , Er ¹⁶⁶ , Tm ¹⁶⁹ , Yb ¹⁷³ , Lu ¹⁷⁵ , Hf ¹⁷⁹ , Ta ¹⁸¹ , Pb ²⁰⁸ , Th ²³² , U ²³⁸	Li ⁷ , Ca ⁴³ , Sc ⁴⁵ , Ti ⁴⁹ , V ⁵¹ , Cr ⁵² , Mn ⁵⁵ , Co ⁵⁹ , Ni ⁶⁰ , Cu ⁶⁵ , Zn ⁶⁶ , Ga ⁷¹ , Rb ⁸⁵ , Sr ⁸⁸ , Y ⁸⁹ , Zr ⁹⁰ , Nb ⁹³ , Mo ⁹⁵ , Sn ¹¹⁸ , Cs ¹³³ , Ba ¹³⁷ , La ¹³⁹ , Ce ¹⁴⁰ , Pr ¹⁴¹ , Nd ¹⁴³ , Sm ¹⁴⁷ , Eu ¹⁵¹ , Gd ¹⁵⁵ , Tb ¹⁵⁹ , Dy ¹⁶³ , Ho ¹⁶⁵ , Er ¹⁶⁶ , Tm ¹⁶⁹ , Yb ¹⁷³ , Lu ¹⁷⁵ , Hf ¹⁷⁹ , Ta ¹⁸¹ , Pb ²⁰⁸ , Th ²³² , U ²³⁸	Li ⁷ , Be ⁹ , Mg ²⁵ , Si ³⁰ , P ³¹ , Ca ⁴³ , Sc ⁴⁵ , Ti ⁴⁹ , V ⁵¹ , Cr ⁵² , Mn ⁵⁵ , Co ⁵⁹ , Ni ⁶⁰ , Cu ⁶⁵ , Zn ⁶⁶ , Ga ⁷¹ , Rb ⁸⁵ , Sr ⁸⁸ , Y ⁸⁹ , Zr ⁹⁰ , Nb ⁹³ , Mo ⁹⁵ , Sn ¹¹⁸ , Sb ¹²¹ , Cs ¹³³ , Ba ¹³⁷ , La ¹³⁹ , Ce ¹⁴⁰ , Pr ¹⁴¹ , Nd ¹⁴³ , Sm ¹⁴⁷ , Eu ¹⁵¹ , Gd ¹⁵⁵ , Tb ¹⁵⁹ , Dy ¹⁶³ , Ho ¹⁶⁵ , Er ¹⁶⁶ , Tm ¹⁶⁹ , Yb ¹⁷³ , Lu ¹⁷⁵ , Hf ¹⁷⁹ , Ta ¹⁸¹ , Pb ²⁰⁸ , Th ²³² , U ²³⁸

* teores médios das análises WDS via microsonda eletrônica

V. ANÁLISES ISOTÓPICAS COM ESPECTROMETRIA DE MASSA EM PLASMA DE INDUÇÃO ACOPLADA (MONO-COLETOR) POR ABLASÃO LASER (LA-ICP-MS) E DATAÇÃO U-Pb

Determinações geocronológicas foram efetuadas utilizando a sistemática U-Pb em cristais de zircão do Complexo Morro Redondo, obtidos de amostras representativas dos Plútons Papanduva e Quiriri, de riolito contemporâneo e de outros plútons de interesse para a definição mais adequada da geocronologia da Província Graciosa (Plútons Corupá, Guaraú, Mandira e Alto Turvo).

Os cristais foram separados a partir de *ca.* 3 – 5 kg de amostras de rocha total, seguindo a metodologia de rotina no Centro de Pesquisas Geocronológicas (Cepegeo) do IGc-USP (e.g., Passarelli et al., 2009), que consiste, inicialmente, das seguintes etapas: fragmentação manual > britagem em britador de mandíbulas > moagem em moinho de disco > peneiramento em malhas progressivamente menores. As frações mais finas (100 – 250 mesh) seguiram para etapas de concentração de zircão com o emprego sequencial de: mesa vibratória de Wiffley > separação magnética manual de magnetita > separação das frações de minerais pesados (incluindo zircão) por meio de líquidos pesados (bromofórmio e iodeto de metileno) > limpeza com HNO₃ > separação de frações magnéticas com separador Frantz (correntes de 0,5, 0,7, 0,8 e 1,0 A) > seleção manual sob estereoscópio dos melhores cristais para análise (populações de 15 a 30 cristais por amostra). Completa-se a sequência com a aquisição de imagens SEI e de CL das populações de zircão selecionadas, que serviram, ao lado de imagens óticas sob luz transmitida, de guias para seleção e posicionamento mais adequado dos *spots* analíticos.

As análises geocronológicas U-Pb *in-situ* nos cristais de zircão selecionados foram efetuadas nas dependências do MITERAC da Universidade de Notre Dame, Indiana, EUA, utilizando-se o ICP-MS de setor magnético ThermoFinnigan Element2 acoplado ao sistema de ablação a laser UP213 da ESI-New Wave. As análises de ablação foram efetuadas com um diâmetro do laser de 30 µm, focado na superfície do cristal, a uma frequência de 4 Hz e energia

nominal de saída de 55%, o que corresponde a uma fluência entre 4 e 5 J/cm². As análises individuais foram completadas após 75 s, divididos em 30 s para leitura do *background*, seguidos de 30 s de ablação a laser no cristal e 15 s de *washout*. Foram quantificados os íons ²⁰⁴(Pb+Hg), ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, ²³⁵U, ²³⁸U e ²³²Th¹⁶O. O sinal de ²⁰²Hg foi medido para monitorar a interferência de ²⁰⁴Hg no sinal do ²⁰⁴Pb, adotando-se o valor de ²⁰⁴Hg/²⁰²Hg de 0,229883 (Simonetti & Neal, 2010).

O monitoramento do *drift* instrumental e a correção de fracionamento elementar por indução a laser (*laser induced elemental fractionation – LIEF*) foram realizados com o emprego de técnica conhecida como “*standard-sample bracketing*” (e.g. Simonetti & Neal, 2010; Sobrinho et al., 2011; Chen & Simonetti, 2012): uma série de cinco medidas no zircão de padrão internacional BR266 (idades ²⁰⁶Pb/²³⁸U = 559 ± 0.2 Ma e ²⁰⁷Pb/²⁰⁶Pb = 562.6 ± 0.2 Ma, Stern & Amelin, 2003) foi efetuada a cada 15 determinações de idade nos cristais de zircão estudados. A redução dos dados seguiu o procedimento descrito em Simonetti et al. (2005), que possibilita a correção dos valores de Pb comum através das flutuações observadas no padrão BR266. A diagramação dos resultados e obtenção de idades concórdia foi efetuada com o programa Isoplot, em suas versões 4.0 e 3.7 (Ludwing, 2003), considerando-se 95 % para o intervalo de confiança.

Um total de 11 amostras, sendo cinco provenientes do Complexo Morro Redondo, foi analisado, totalizando cerca de 350 determinações individuais em cristais de zircão.

VI. ANÁLISES ISOTÓPICAS Lu-Hf COM ESPECTROMETRIA DE MASSA EM PLASMA DE INDUÇÃO ACOPLADA (MULTI-COLETOR) POR ABLAÇÃO A LASER (LA-MC-ICP-MS)

Determinações *in-situ* de isótopos de Hf em cristais de zircão de quatro amostras representativas dos Plútons Papanduva (uma amostra) e Quiriri (duas amostras), além do riolito contemporâneo (uma amostra) foram realizadas nas dependências do MITERAC, Universidade de Notre Dame, EUA, utilizando o equipamento multicoletor (MC) de ICP-MS NuPlasma II da Nu Instruments, acoplado a um sistema de ablação a laser Excimer NWR-193nm da ESI-New Wave.

As análises foram conduzidas com diâmetro do laser de 50 μm a uma frequência de 10 Hz e energia de saída correspondente a uma fluência de ca. 14 J/cm². O fluxo de He na câmara de ablação foi mantido a uma taxa de ca. 0,20 L/minuto. As razões isotópicas foram determinadas usando todo o arranjo de coletores Faraday, com aquisição simultânea dos íons ¹⁷¹Yb, ¹⁷²Yb, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁷⁶Hf, ¹⁷⁷Hf, ¹⁷⁸Hf, ¹⁷⁹Hf e ¹⁸⁰Hf. Para as correções da interferência do sinal de ¹⁷⁶Lu sobre ¹⁷⁶Yb e ¹⁷⁶Hf assumiu-se um viés instrumental de massa para o Lu = Yb = Hf, como discutido em Pearson et al. (2008). A redução dos dados envolveu o uso do programa *Time Resolved Analysis* (TRA) da Nu Instruments, com cada análise individual consistindo de 45 s para medição da linha de base, seguidos por um intervalo de ablação entre 45 e 100 s. A reprodutibilidade externa e validação do protocolo analítico empregado foi confirmada a partir de repetidas análises dos padrões internacionais de zircão Mud Tank (n = 19) e 91500 (n = 10), resultando em valores médios da razão ¹⁷⁶Hf/¹⁷⁷Hf de $0,28248 \pm 0,00006$ (2 σ) e $0,28228 \pm 0,00002$ (2 σ), respectivamente, ambos em excelente concordância os valores definidos em literatura de $0,282504 \pm 0,000044$ (2 σ) para o Mud Tank (Woodhead & Hergt, 2005) e $0,282308 \pm 0,000006$ (2 σ) para o 91500 (Blichert-Toft, 2008).

Para o cálculo dos parâmetros $\mathcal{E}\text{Hf}(0)$ e $\mathcal{E}\text{Hf}(t)$, onde t representa a idade de cristalização da rocha, neste caso fixada em 580 Ma a partir das determinações ²⁰⁶U/²³⁸Pb por LA-ICP-MS (ver item V), foram utilizadas as razões ¹⁷⁶Hf/¹⁷⁷Hf = 0,282772 e ¹⁷⁶Lu/¹⁷⁷Hf = 0,033200 referentes ao reservatório condrítico original (CHUR) no presente dia de Blichert-Toft & Albarède (1997) e a constante de decaimento $\lambda(^{176}\text{Lu}) = 1,867 \times 10^{-11} \text{ anos}^{-1}$ de Söderlund et al. (2004). As idades modelo foram computadas em relação ao manto empobrecido (DM), utilizando-se para tal as razões $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{DM},0} = 0,283225$ e $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM},0} = 0,038512$ de Vervoort & Blichert-Toft (1999), considerando-se modelos de evolução em um e dois estágios. Neste último caso, o fator de enriquecimento $f_{\text{Lu/Hf}} = 0,015$ correspondente ao valor da "bulk earth" (cf. Goodge & Vervoort, 2006) foi adotado.

Foram efetuadas cerca de 50 determinações pontuais em cristais de zircão, em cima ou próximas das determinações com finalidades geocronológicas. Cumpre destacar, entretanto, que os volumes analisados foram maiores, menores ou similares.

VII. ANÁLISES DE ISÓTOPOS DE OXIGÊNIO COM FLUORINIZAÇÃO COM LASER

Razões isotópicas *in-situ* de O em anfibólios, clinopiroxênios, quartzo e feldspatos em amostras dos Plútons Papanduva e Quiriri foram determinadas nos laboratórios do CEST (*Center for Environmental Science and Technology*) da Universidade de Notre Dame, EUA, que conta com sistema de fluorinização assistida por laser MIR-10 da ESI-New Wave acoplado a uma linha de extração de O para silicatos configurada de acordo com a metodologia de Sharp (1990). As razões isotópicas de O foram medidas com o espectrômetro de massa Delta V Plus da Thermo Fischer Scientific

O método de fluorinização a laser de Sharp (1990) envolve o aquecimento dos minerais em câmara de amostras preenchida com F, utilizando-se de laser de CO₂, atuante na faixa do infravermelho. Grãos/fragmentos de silicatos em populações de ca. 0,6 a 3 mg são depositados em orifícios individuais de um porta-amostras de Ni. Este porta-amostras é então colocado em uma câmara coberta por uma placa de BaF₂, transparente nas regiões do visível e do infravermelho e não reativa com F. Na sequência, injeta-se BrF₂ duplamente destilado na câmara. Com a elevação da temperatura causada pela incidência do laser, a amostra reage e libera O₂ juntamente com outros gases (e.g., SiF₄ em quartzo). As linhas de extração consistem de tubos de aço inerte com extremidades que permitem aquecimento e resfriamento simultâneo para a purificação do O₂ que é então sequestrado e congelado em frasco de quartzo contendo pequenas esferas de zeólitas. Este frasco é posteriormente aquecido, liberando o O₂ que é conduzido para o espectrômetro de massa com uma corrente de gás He. Uma mistura de O₂ + He entra então em uma coluna cromatográfica de gás conectada diretamente à entrada do espectrômetro, onde é finalmente quantificado.

O fracionamento instrumental das razões isotópicas de ¹⁸O/¹⁶O foi monitorado por meio de repetidas análises no padrão sintético de quartzo Lausanne, com valor certificado de ¹⁸O/¹⁶O de 18,15‰ (Jourdan et al., 2009).

Foram realizadas 42 análises em frações de quartzo, feldspato alcalino, plagioclásio, piroxênios, anfibólios e zircão, obtidas por moagem manual e cuidadosa separação em lupa estereoscópica.

VIII. ANÁLISES GEOQUÍMICAS EM ROCHA TOTAL

Dados geoquímicos incluindo elementos maiores, menores e traços em rocha-total de amostras representativas das principais variedades petrográficas dos Plútons Papanduva e Quiriri foram obtidos nas dependências dos Laboratórios de Química e ICP-AES/MS e de Fluorescência de Raios-X do GMG-IGc/USP.

As amostras foram previamente preparadas no Laboratório de Tratamento de Amostras (LTA) do IGc-USP, seguindo-se as etapas usuais de fragmentação com marreta e martelo, britagem em britador primário de mandíbulas de aço, prensa hidráulica e moagem em moinho de ágata do tipo planetário por cerca de 20 minutos, atingindo granulometria menor que 200 mesh. Seguiu-se a preparação de pastilhas prensadas e fundidas a partir do material pulverizado (cf. Sertek, 2010).

VIII.1. ELEMENTOS MAIORES, MENORES E TRAÇOS COM FLUORESCÊNCIA DE RAIOS X

A quantificação dos elementos maiores, menores e alguns traços (e.g., Rb, Sr, Zn, Zr) foi realizada através de Fluorescência de Raios-X em pastilhas prensadas e fundidas, utilizando-se do equipamento Philips, modelo PW2400, do Laboratório de Fluorescência de Raios-X do IGc-USP, seguindo os protocolos analíticos de rotina deste laboratório (e.g. Mori et al., 1999).

Foram obtidas 31 análises em rocha total por este método.

VIII.2. ELEMENTOS TRAÇOS COM ESPECTROMETRIA DE PLASMA

Os demais elementos traços de 20 amostras selecionadas foram determinados por espectrometria de plasma (ICP-MS), utilizando o espectrômetro quadrupolo MS-ELAN 6100 DRC da Perkin Elmer. A preparação das amostras seguiu o método da digestão ácida em bombas do tipo Parr, usando HNO_3 e HF concentrados sob temperaturas de ca. 200 °C por cinco dias, de maneira a se obter dissolução completa de minerais de menor solubilidade, como o zircão. Detalhes dos procedimentos e das rotinas analíticas atualmente disponíveis no laboratório de Química e ICP-AES/MS do GMG-IGc-USP são descritos em detalhe por Navarro et al. (2008).

IX. ANÁLISES ISOTÓPICAS Rb-Sr E Sm-Nd

Amostras representativas foram selecionadas para estudos isotópicos em rocha total pelas sistemáticas Rb-Sr e Sm-Nd. As análises foram efetuadas no Cepegeo (IGc-USP), em Espectrômetro de Massa VG 354 e ThermoFinnigan MAT 262, seguindo os procedimentos e protocolos analíticos de rotina (e.g. Sato et al., 1995). A preparação foi semelhante à abertura das amostras para análises via ICP-MS descritas acima, utilizando-se, contudo, um período de digestão ácida de 10 dias a 160 °C. Colunas de troca catiônica preenchidas com resina AG-50 (200 – 400 mesh) foram empregadas para as etapas de separação isotópica, usando água e HCl em concentrações variáveis. O Sr foi extraído com HCl a 2,5N, gerando um resíduo que foi posteriormente lavado com HCl a 6,2 N para extração dos elementos terras-raras e separação de Sm e Nd em colunas preenchidas com pós de teflon e lavagem em HCl a 0,26 e 0,55 N, com menor concentração destinada à extração de Nd. Devido as baixas concentrações de Sr na maioria das amostras, as determinações isotópicas deste elemento foram efetuadas através do método de diluição isotópica, conforme rotina do laboratório para estas situações.

Os padrões internacionais NBS-987 e La Jolla foram empregados para as determinações Rb-Sr e Sm-Nd, respectivamente, juntamente com as razões normalizadoras $^{86}\text{Sr}/^{88}\text{Sr} = 0,1194$ (Steiger & Jäeger, 1978) e $^{146}\text{Nd}/^{144}\text{Nd} = 0,7219$ (Michard et al., 1985)

As razões $\epsilon\text{Nd}(0)$ foram calculadas em relação ao CHUR, utilizando-se a razão $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR},0} = 0,512638$ de Hamilton et al. (1983). As razões $\epsilon\text{Nd}(t)$ foram derivadas com base na idade $^{206}\text{U}/^{238}\text{Pb}$ de cristalização dos plútons (fixada em 580 Ma) e razões Sm/Nd obtidas das análises químicas em rocha-total por ICP-MS. As idades modelo T_{DM} foram computadas a partir dos parâmetros apresentados por DePaolo (1988) e DePaolo et al. (1991): $a = 0,25$, $b = -3$; $c = 8,5$ e $\lambda = 6,54 \times 10^{-12} \text{ anos}^{-1}$.

Foram obtidos dados isotópicos para Sr e Nd em oito amostras, representativas das principais variedades amostradas dos plútons Papanduva e Quiriri.

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PARTE III

DISCUSSÕES PRELIMINARES SOBRE ÁREAS-FONTES

I. CONSIDERAÇÕES INICIAIS

Os modelos petrogenéticos propostos para a formação de granitos de tipo-A podem ser agrupados em três grupos (Eby, 2006): 1) geração a partir da diferenciação de magmas de origem *mantélica* isotopicamente semelhantes aos basaltos de ilhas oceânicas (OIB), com diferentes graus de *contaminação e assimilação crustal*; 2) diferenciação de magmas toleíticos continentais, com diferentes proporções de *interação crustal*; 3) fusão parcial de *fonte crustal* empobrecida por eventos prévios de fusão. Vilalva (2007) apresenta uma extensa revisão sobre os principais pontos de cada um desses grupos de modelos. As considerações mais pertinentes de cada grupo detalhados nessa revisão são colocadas a seguir e servirão para embasar as discussões preliminares sobre as áreas-fontes possivelmente envolvidas na geração das rochas graníticas do Complexo Morro Redondo.

I.1. FONTES MANTÉLICAS

Granitos de tipo-A de composição peralcalina (associação alcalina) e rochas intermediárias e máficas associadas possuem, em geral, razões isotópicas ($^{87}\text{Sr}/^{86}\text{Sr}$)₀ relativamente baixas e valores de ϵNd homogêneos em escala de intrusão, positivos ou pouco negativos. As razões isotópicas de Sr e Nd encontradas por Turner et al. (1992) para granitos peralcalinos da Austrália, e por Waight et al. (1998) para o granito French Creek (Nova Zelândia), por exemplo, são semelhantes aos das rochas básicas coexistentes, o que sustentaria a formação dos magmas de tipo-A a partir da cristalização fracionada de magmas basálticos, originados de fusão por decompressão de um manto de composição semelhante aos OIB (e.g. Loiselle & Wones, 1979; Eby, 1992; Bonin, 1996; Trumbull et al., 2004). A eficiência da cristalização fracionada de magmas

basálticos originando magmas traquíticos e riolíticos metaluminosos é bem conhecida em alguns riftes continentais e em áreas oceânicas (e.g. Avanzinelli et al., 2004; Martin, 2006).

I.2. CONTAMINAÇÃO CRUSTAL

Muitos corpos graníticos de tipo-A possuem assinaturas isotópicas que indicam participação de componentes crustais na gênese dos magmas de tipo-A. Poitrasson et al. (1995) sugerem que as baixas razões isotópicas iniciais de Sr e os valores positivos ou pouco negativos de ϵNd nos granitos da Córsega seriam indicativos de uma fonte mantélica isotopicamente homogênea. Os valores de $\delta^{18}\text{O}$ significativamente mais altos que os valores mantélicos típicos e a heterogeneidade dos valores de ϵNd neste caso refletiriam proporções variadas de assimilação crustal por parte de magmas mantélicos (cf. também Marks et al., 2003). Neste contexto, granitos de tipo-A metaluminosos representariam o produto da contaminação crustal intensa de magmas peralcalinos (Poitrasson et al., 1995; Rossi & Cocherie, 1987; Volkert et al., 2000; Vander Auwera et al., 2003).

Bowden & Kinnaird (1978) apontam para a possibilidade da geração de magmas graníticos a partir do fracionamento de magmas mantélicos. Esses magmas graníticos poderiam então originar duas suítes de rochas, uma mais peralcalina e outra mais aluminosa, por diferentes reações *subsolidus*, na presença de fluidos hidrotermais. Seguindo este raciocínio, Qiu et al. (2004) sugerem que as diferenças mineralógicas e geoquímicas existentes entre os granitos das associações aluminosa e alcalina são geradas via diferentes caminhos de diferenciação, controlada pela variação nos teores de F de um magma mantélico em comum. De fato, muitos são os exemplos onde granitos da associação aluminosa coexistentes com variedades da associação alcalina (e.g. Rio Ulungur, China; Tin Zebane, Argélia; French Creek, Nova Zelândia; Complexo Brandberg, Namíbia), com valores de ϵNd e Sr_i e padrões de traços e ETR semelhantes. Nesta situação, a fusão parcial de fontes mantélicas gerariam magmas da associação aluminosa, sem contaminação crustal importante e com altos graus de cristalização fracionada, como acontece nos

granitos da associação alcalina (Hadj-Kaddour et al., 1998; Schmitt et al., 2000; Litvinovsky et al., 2002).

Fonte mantélica comum tem sido usada também para explicar a justaposição de granitos de tipo-A com rochas subsaturadas em sílica (e.g. nefelina-sienitos) em um mesmo complexo. Neste caso, a formação dos magmas de tipo-A envolveria forte assimilação crustal combinada com cristalização fracionada (Foland et al., 1993). Upton et al. (2003), sugerem que a evolução magmática principal da Província Gardar envolve diferenciação de magmas básicos alcalinos até resíduos fonolíticos, com a geração dos magmas graníticos envolvendo altos graus de assimilação crustal acompanhada por cristalização fracionada, uma ideia que torna-se mais plausível ao se assumir uma crosta contaminante metassomatizada, ou áreas fontes mantélicas com períodos prévios de fertilização (Macdonald & Upton, 1993; Martin, 2006).

I.3. FONTES CRUSTAIS

Em maciços metaluminosos e peraluminosos, os valores negativos e heterogêneos de ϵ_{Nd} e as altas razões $(^{87}\text{Sr}/^{86}\text{Sr})_0$, tipicamente crustais, além dos teores mais elevados de Zr, Eu, Rb, Sr e Al não são satisfatoriamente explicados por cristalização fracionada intensa de magmas básicos com contaminação crustal, mas sim através da anatexia de crosta inferior heterogênea, de assinatura peraluminosa (Rämö & Haapala, 1995; King et al., 1997; Dall'Agnol et al., 1999). Esse modelo é contundente no caso de corpos graníticos de tipo-A com altos valores de $\delta^{18}\text{O}$, gerados por fusão parcial de crosta inferior em episódios de distensão logo após eventos orogenéticos, onde rochas básicas de derivação mantélica são ausentes (e.g. Nédélec et al., 1995). Para Creaser et al. (1991) e outros, uma fonte crustal ideal para a geração de magmas graníticos de tipo-A aluminosos tem composição tonalítica a granodiorítica (e.g. Anderson & Bender, 1989; Poitrasson et al., 1995; King et al., 1997; Dall'Agnol et al., 2005). Experimentos de fusão parcial dessas rochas conduzidos por Patiño Douce (1997) reproduziram com sucesso algumas características típicas dos granitos de tipo-A metaluminosos em condições redutoras e anidras a 950 °C de temperatura e

pressão de 4 kbar. Para o autor, o ambiente extensional de formação desses granitos favoreceria a colocação de magmas básicos mantélicos como fonte de calor para a fusão da crosta superior.

I.4. METASSOMATISMO CRUSTAL

Um modelo genético universal através de fusão de crosta metassomatizada por fluidos mantélicos, com fracionamento concomitante de magmas basálticos, uma extensão lógica do conceito de metassomatismo regional de um manto estéril em zonas de rifte, é colocado em diversos trabalhos (e.g. Harris & Marriner, 1980; Adbel-Rahman & Martin, 1990; Maheshwari et al., 2001; Adbel-Rahman & El-Kibbi 2001, Martin 2006, Katzir et al., 2007). Esse modelo se baseia no fato de que ambientes em regimes extensivos têm o transporte vertical de fluidos quentes mantélicos como o principal mecanismo de transferência de calor. Fluidos esses ricos em álcalis e sílica (além de H_2O e CO_2 em proporções variadas), capazes de transportar elementos HFS, incluindo ETRs, causando assim um metassomatismo regional da crosta inferior, conforme ascendem, podendo transformar completamente sua composição, homogeneizando as assinaturas isotópicas e geoquímicas, em um sistema aberto (Preston et al., 2003). Como explica Martin (2006), a ascensão diapírica de magmas basálticos do manto pode ocorrer paralelamente ao metassomatismo, fornecendo calor para a fusão da crosta agora fértil. Assim, dois eventos podem ocorrer simultaneamente: 1) a fusão da crosta originando magmas peralcalinos a metaluminosos e mesmo peraluminosos de tipo-A, e ainda magmas subsaturados em sílica e carbonatíticos, dependendo das proporções de H_2O e CO_2 nos fluidos metassomatizantes; e 2) a cristalização fracionada dos magmas basálticos resultando em granitos e riolitos de tipo-A com assinatura mantélica e rochas básicas eventualmente associadas. Misturas entre esses dois tipos de magma gerados podem ocorrer, bem como a assimilação crustal dos magmas mantélicos, resultando em rochas com assinaturas crustais e mantélicas.

II. ÁREAS-FONTES DO COMPLEXO MORRO REDONDO: EVIDÊNCIAS ISOTÓPICAS

II.1. ISOTOPIA Rb-Sr E Sm-Nd EM ROCHA TOTAL

Determinações isotópicas para as sistemáticas Rb-Sr e Sm-Nd foram realizadas em amostras selecionadas dos Plútons Papanduva e Quiriri. Os detalhes analíticos são apresentados na Parte II, item IX e os resultados encontram-se listados nas tabelas 3 e 4 do Anexo V. Vale mencionar que dados isotópicos de Sr e Nd estão disponíveis em número muito reduzido para o Complexo Morro Redondo. A maior parte dos dados refere-se à sistemática Rb-Sr (Siga Jr., 1995; Kaul, 1997), e apenas um dado foi obtido para a sistemática Sm-Nd (Siga Jr., 1995).

A evolução isotópica do Sr é extremamente complexa em granitos de tipo-A, particularmente das variedades peralcalinas, devido à mobilidade dos elementos Rb e Sr durante a evolução tardi- a pós-magmática dessas rochas. Os resultados obtidos para a sistemática Rb-Sr refletem esse problema e muitas das amostras registram valores das razões $\text{Sr}^{87}/\text{Sr}^{86}$ no tempo presente (0) e há 580 Ma (t) que são, de fato, irreais. Por exemplo, para o Plúton Papanduva, onde a situação é mais crítica, os teores de Sr das amostras investigadas são extremamente baixos, variando entre 2,8 e 5,5 ppm, enquanto as razões $(^{87}\text{Sr}/^{86}\text{Sr})_t$ calculadas são muito altas, variando entre 0,73496 e 1,35074, discordando sobremaneira das estimativas disponíveis em literatura, que apontam para razões $(^{87}\text{Sr}/^{86}\text{Sr})_t$ da ordem de 0,714 para esse Plúton (e.g. Siga Jr, 1995; Kaul, 1997).

Os resultados para o Plúton Quiriri são mais satisfatórios. As razões $^{87}\text{Sr}/^{86}\text{Sr}$ iniciais neste caso variam entre 0,7125 a 0,7075, com uma amostra (MR-174) registrando ainda um valor mais baixo de 0,7028, similar aos valores disponíveis em literatura, da ordem de 0,702 (e.g. Siga Jr, 1995; Kaul, 1997).

Os isótopos de Nd, por sua vez, se mostraram mais favoráveis aos estudos petrogenéticos e à caracterização de possíveis áreas-fontes. Para o Plúton Papanduva, foram analisadas amostras referentes às quatro facies petrográficas mapeadas (ver Anexo IV-A). No geral, as principais variações são registradas entre as fácies maciça e a fácies protomilonítica. Assim, os

valores da razão Sm/Nd (ppm) entre 0,186 e 0,267, aumentando dos granitos maciços para os protomiloníticos (ver Anexo IV-A). Da mesma forma, o fator de enriquecimento $f_{\text{Sm/Nd}}$ é bastante variável, desde -0,18 nesses a -0,43 naqueles. No Plúton Quiriri, os valores registrados são bem homogêneos e as variações são muito restritas. As amostras investigadas mostram razão Sm/Nd entre 0,175 e 0,188 e $f_{\text{Sm/Nd}}$ entre -0,42 e -0,46.

Os valores de $\epsilon\text{Nd}(t)$ (onde $t = 580$ Ma) são sempre negativos e distintos para os dois plútons. Para o Plúton Papanduva, os valores variam entre -15,6 e -16,3, sendo ligeiramente menos negativos do que aqueles verificados no Plúton Quiriri, entre -18,8 e -20,5. A Figura 2 mostra a variação do $\epsilon\text{Nd}(t)$ em função do teor de SiO_2 da rocha. Observa-se uma tendência de aumento de $\epsilon\text{Nd}(t)$ em direção a composições mais ricas em sílica no Plúton Quiriri, uma situação muito distinta da verificada no Plúton Papanduva, onde o aumento dos teores de SiO_2 não é acompanhada de variações significativas de $\epsilon\text{Nd}(t)$.

Figura 2: Diagrama binário SiO_2 x $\epsilon\text{Nd}(t)$ para amostras dos Plútons Papanduva (vermelho) e Quiriri (azul) do Complexo Morro Redondo.

As idades-modelo T_{DM} calculadas, que sugerem o período em que os protólitos das rochas graníticas foram diferenciados do manto e incorporados à crosta continental, são plotadas no diagrama da Figura 3, que mostra a evolução de ϵNd ao longo do tempo. Com exceção de duas

amostras do Plúton Papanduva, que registram idades T_{DM} muito mais antigas, da ordem de 4,1 a 3,6 Ga, os resultados são semelhantes para ambos os plútons, variando entre 2,8 e 2,4 Ga no Plúton Papanduva e 2,4 a 2,7 Ga no Plúton Quiriri e se sobrepõem de maneira clara às idades T_{DM} para rochas do embasamento da Microplaca Luiz Alves (Complexo Granulítico Santa Catarina, e.g. Basei et al., 2008).

As idades-modelo calculadas são confrontadas com os valores do fator de enriquecimento $f_{Sm/Nd}$ na Figura 4. Nota-se que as amostras do Plúton Papanduva que registram T_{DM} anormalmente altas são as que também possuem os maiores valores de $f_{Sm/Nd}$. Essas amostras são representativas das fácies protomilonítica e microgranítica e, curiosamente, são as que possuem os menores teores de SiO_2 . Tal fato deve refletir alterações nas razões Sm/Nd causadas, por exemplo pelo fracionamento de fases acessórias que incorporam elementos terras-raras (ETR), em especial os leves e médios. De fato, a amostra MR-01D, que registra uma T_{DM} de 3,6 Ga (Figs. 3 e 4) provém da fácies microgranítica, interpretada como uma das fases finais no magmatismo do Complexo Morro Redondo (ver Anexo IV-A). Ao microscópio, essa amostra revela a presença de chevkinita e zircão. Por sua vez, a amostra MR-50 (A+) se refere a um álcali-feldspato granito protomilonítico. Além da deformação superimposta, essa amostra é caracterizada pela presença relativamente comum de uma série de minerais acessórios raros, muitos deles portadores de ETR e elementos HFS, tais como narsarsukita, britholita, elpidita e outros zirconossilicatos de (Na, K) e astrofilita (ver, por exemplo, Anexos IV-D, IV-E).

Figura 3: Diagrama binário de evolução do ϵNd ao longo do tempo para amostras do Complexo Morro Redondo. Note a boa sobreposição entre as idades T_{DM} calculadas para o Complexo Morro Redondo e aquelas disponíveis para o embasamento da Microplaca Luiz Alves (cf. Basei et al., 2008).

Figura 4: Diagrama binário $f_{(Sm/Nd)} \times T_{DM}$ para amostras do Complexo Morro Redondo. Símbolos como na Figura 2.

II.2. ISOTOPOS DE Hf EM ZIRCÃO

Isótopos de Hf foram determinados para uma amostra da fácies maciça do Plúton Papanduva (MR-39), duas amostras do Plúton Quiriri (MR-161 e MR-186A) e para riolito associado. Os resultados aparecem listados na Tabela 15 do Anexo V.

As Figuras 5 a 7 apresentam histogramas com a média ponderada das razões $^{176}\text{Hf}/^{177}\text{Hf}$ determinadas em zircões dessas amostras. Os valores dessa razão variam entre 0,28188 – 0,28203, com média ponderada em $0,28197 \pm 0,000031$ para o Plúton Papanduva (Fig. 5), entre 0,28143 – 0,28201, com média ponderada em $0,28169 \pm 0,000054$ para o Plúton Quiriri (Fig. 6) e entre 0,28182 – 0,28198, com aparentemente duas populações de valores próximas, com médias ponderadas de $0,28185 \pm 0,000018$ e $0,28194 \pm 0,000042$ (Fig. 7)

Os valores calculados de $\varepsilon\text{Hf}(t)$, onde $t = 580$ Ma, são sempre negativos e dispersos. A Figura 8 mostra a variação de $\varepsilon\text{Hf}(t)$ em função do fator de enriquecimento $f_{\text{Lu/Hf}}$. Nota-se uma boa correlação positiva entre esses parâmetros para os zircões do Plúton Papanduva e do riolito, que registram, respectivamente, $\varepsilon\text{Hf}(t)$ entre -14,8 a -20,0 (valor médio de -17,1) e -16,3 a -21,4 (valor médio de -19,2). O Plúton Quiriri é menos radiogênico e caracterizado por um comportamento distinto do $\varepsilon\text{Hf}(t)$ que varia em um longo intervalo desde -14,8 até -34,1 (valor médio de -25,8), porém sem experimentar variações significativas para $f_{\text{Lu/Hf}}$.

Os valores de $\varepsilon\text{Hf}(0)$ e $\varepsilon\text{Hf}(t)$ são unidos por linhas paralelas no diagrama de evolução da Figura 9, o que pode indicar evolução isotópica em sistema fechado desde a cristalização até o presente dia (e.g. Goodge & Vervoort, 2006). Essas linhas são projetadas para a curva de evolução do manto empobrecido (DM) usando um fator de enriquecimento $f_{\text{Lu/Hf}} = 0,015$ (cf. Goodge & Vervoort, 2006) resultando em idades T_{DM} entre 2,5 e 3,1 Ga; as mais antigas registradas para o Plúton Quiriri e as mais novas para o Papanduva. O riolito possui uma T_{DM} de 2,7 Ga, muito próxima àquela computada para o Plúton Papanduva. Em princípio, essas idades corresponderiam à idade da crosta na qual os granitos foram colocados (cf. Goodge & Vervoort, 2006), de maneira que é válido afirmar que granitos mais radiogênicos do Plúton Papanduva estão associados com

rochas encaixantes mais jovens, enquanto que o Plúton Quiriri, menos radiogênico, é intrusivo em rochas mais antigas.

Figura 5: Histograma e média ponderada das razões $^{176}\text{Hf}/^{177}\text{Hf}$ medidas em cristais de zircão da fácies maciça do Plúton Papanduva

Figura 6 Histograma e média ponderada das razões $^{176}\text{Hf}/^{177}\text{Hf}$ medidas em cristais de zircão do Plúton Quiriri

Figura 7: Histograma e média ponderada das razões $^{176}\text{Hf}/^{177}\text{Hf}$ medidas em cristais de zircão de riolito associado do Complexo Morro Redondo

Figura 8: Diagrama isotópico binário $\epsilon\text{Hf}(t)$ x $f_{\text{Lu}/\text{Hf}}$ para cristais de zircão dos plútons Papanduva e Quiriri e riolito associado do Complexo Morro Redondo

Figura 9: Diagrama isotópico binário $\epsilon_{\text{Hf}}(t)$ x $f_{\text{Lu/Hf}}$ para cristais de zircão dos plútons Papanduva e Quiriri e riolito associado do Complexo Morro Redondo

II.3. ISÓTOPOS ESTÁVEIS DE O

Adicionalmente, razões isotópicas $^{18}\text{O}/^{16}\text{O}$ para frações de zircão foram determinadas nas amostras investigadas pela sistemática Lu-Hf. Os valores encontram-se na Tabela 16 do Anexo V, juntamente com outros minerais. A Figura 10 compara as razões obtidas com os valores de $\epsilon_{\text{Hf}}(t)$ (Fig. 10A) e idades T_{DM} calculadas em zircão das mesmas amostras. É interessante notar que, com exceção de uma amostra do Plúton Quiriri (MR-161), que registra um valor de 8,5 ‰, as razões $\delta^{18}\text{O}$ medidas são equivalentes, variando entre 4,8 e 6,0 ‰, próximas aos valores típicos encontrados em zircões mantélicos (e.g. Valley et al., 2003), o que sugere participação mantélica na geração dos magmas graníticos que culminaram na formação dos Plútons Papanduva e Quiriri.

Figura 10: Comparação entre razões $^{18}\text{O}/^{16}\text{O}$ (‰, VSMOW) determinadas em frações de zircão do Complexo Morro Redondo com (A) $\epsilon\text{Hf}(t)$ e (B) T_{DM} . Símbolos como na Figura 8. Campo dos zircões mantélicos segundo Valley et al. (2003).

III. CONSIDERAÇÕES FINAIS

A análise conjunta dos dados isotópicos de Sm em rocha-total e Hf e O em cristais de zircão permite traçar algumas considerações ainda preliminares sobre as áreas-fontes envolvidas na geração dos granitos do Complexo Morro Redondo.

Os granitos do Plúton Papanduva e Quiriri possuem valores de $\epsilon\text{Nd}(t)$ sempre negativos (o que pode sugerir contaminação crustal) e relativamente próximos, não havendo, contudo, sobreposição de dados (i.e. Papanduva: -15,6 a -16,3; Quiriri: -18,8 a -20,5, Fig. 2). De fato, como ilustra a Figura 2, a variação dos valores de $\epsilon\text{Nd}(t)$ nesses dois plútons é distinta, aumentando em relação aos teores de SiO_2 no Plúton Quiriri e permanecendo relativamente constante para diferentes teores de SiO_2 no Papanduva. Por outro lado, com exceção das amostras MR-01D e MR-50 (A+) do Plúton Papanduva (ver discussão no subitem II.1) as idades-modelo calculadas com referência ao manto empobrecido (T_{DM}) são idênticas para os dois plútons, variando entre 2,4 e 2,8 Ga. A sobreposição dessas idades com aquelas determinadas para rochas do embasamento da

Microplaca Luiz Alves é sugestiva do envolvimento de uma mesma crosta Paleoproterozoica na gênese desses granitos, de composição isotópica muito evoluída.

A apreciação dos dados de Lu-Hf traz algumas inferências interessantes. Assim como observado para o $\epsilon\text{Nd}(t)$, há uma clara distinção entre os Plútons Papanduva e Quiriri quanto à variação de $\epsilon\text{Hf}(t)$ em relação ao fator de enriquecimento $f_{\text{Lu/Hf}}$. Quando calculadas, as idades T_{DM} para o Plúton Papanduva (i.e. 2,5 Ga) se mostram semelhantes às aquelas obtidas pela sistemática Sm-Nd (i.e. 2,4 – 2,8 Ga), embora sejam algo mais antigas (3,0 Ga) no caso do Plúton Quiriri (T_{DM} Sm-Nd: 2,4 – 2,7 Ga). De fato, por serem menos suscetíveis a processos de intemperismo, deformação ou alteração hidrotermal, os isótopos de Hf registram com maior segurança e resolução informações sobre áreas-fontes e história evolutiva dos magmas (e.g. Hawkesworth & Kemp, 2006).

Por fim, os valores relativamente semelhantes de $\delta^{18}\text{O}$ dos Plútons Papanduva e Quiriri e que se sobrepõem aos valores típicos de zircão mantélico, são indicativos de participação do manto, nos processos genéticos do granitos do Plúton Papanduva, possivelmente como área-fonte.

Assim, as evidências isotópicas descritas parecem sugerir uma área-fonte mantélica única na gênese do Complexo Morro Redondo, com as diferenças geoquímicas e isotópicas refletindo diferentes graus de contaminação por rochas paleoproterozoicas de níveis crustais distintos no embasamento da Microplaca Luiz Alves (e.g. Poitrasson et al., 1995; Vander Auwera et al., 2003).

Tais sugestões são ainda preliminares e carecem de análises sistemáticas mais aprofundadas e detalhadas.

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PARTE IV
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“Geology, petrography and geochemistry of the A-type granites from the The Morro Redondo Complex (PR-SC), South Brazil, Graciosa Province”

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“In-situ U-Pb dating and trace element compositions of zircon from the Graciosa A-type Province, South Brazil: insights for the timing of extensional magmatism at end of the Brasiliano-Pan-African Orogeny”

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ANEXO:

A

GEOLOGY, PETROGRAPHY AND GEOCHEMISTRY OF THE A-TYPE GRANITES FROM THE THE MORRO REDONDO COMPLEX (PR-SC), SOUTH BRAZIL, GRACIOSA PROVINCE.

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ABSTRACT

The Morro Redondo Complex is one of the most important occurrences of the Graciosa A-type Province, S Brazil. The complex is made two distinct granitic plutons, namely Papanduva and Quiriri and contemporaneous bimodal volcanic rocks. The Papanduva Pluton includes massive and deformed peralkaline alkali-feldspar granites with Na-Ca and Na-amphiboles and clinopyroxenes. The deformed types are the most evolved peralkaline rocks in the province and carry rare “agpaitic” minerals, some of them described for the first time in granites from Brazil. The larger Quiriri Pluton is made of massive, slightly peraluminous, biotite syenogranites and monzogranites with rare Ca-amphibole. The biotite compositions from Quiriri are relatively homogeneous, while amphiboles and pyroxenes from Papanduva show increasing Na and Fe³⁺ evolving paths. The Morro Redondo granites are ferroan with high contents of SiO₂, alkalis and HFSE. Within the peralkaline types, which present the highest fe#, the contents of LIL and HFS elements increase with the Agpaitic Index and the most evolved are HHP granites, with radiogenic heat production up to 5.7 μWm⁻³. Geothermobarometric estimates indicate magmatic emplacement under low P (≈ 1 kbar) at temperatures up to 850 – 800 °C, and relatively reduced (QFM) and oxidized (+1 < Δ_{QFM} < +3) for the Papanduva and Quiriri Plutons, respectively. In both cases, melts evolved to relatively high oxidation states as crystallization proceeds.

1. INTRODUCTION

A-type magmatic provinces are widespread distributed in the Earth's crust and were formed since Archaean times as a result of geodynamic processes associated with extensional tectonic environments. A characteristic of the A-type magmatism is the rock type diversity, with contrasting petrographic and geochemical signatures (e.g. Whalen et al. 1987, Eby 1992, Poitrasson et al. 1995, King et al. 1997, Schmitt et al. 2000, Litvinovsky et al. 2002, Gualda and Vlach 2007a,b). The nature of such diversity has been heavily discussed in the literature but still there is not a general consensus on the petrogenetic models and sources involved in their genesis (e.g. Martin 2006, Bonin 2007). The Graciosa Province in south-southern Brazil (Gualda and Vlach 2007a) is a typical example, where A-type granites and syenites from the contrasted aluminous (subalkaline) and alkaline petrographic associations (Lameyre and Bowden 1982, Vlach et al. 1990, King et al. 1997), as well as related K-rich dioritic and some basic and acid volcanic rocks were emplaced during the final stages of the Brasiliano/Pan-Africano Orogeny, at the end of the Neoproterozoic.

The Morro Redondo Complex (Góis 1995) crops out close to the east continental coastal border, between Paraná and Santa Catarina states, south Brazil. It is one of the largest and most important occurrences of A-type granites of the Graciosa Province and is made of granitic rocks of both petrographic associations, as well as coeval bimodal volcanic rocks, being particularly interesting to study the observed petrographic diversity and the genetic relations among these rocks. In this contribution we present and discuss general geologic, petrographic, magnetic susceptibility, as well as mineral and whole-rock chemical data aiming to improve the knowledge of these rocks, to compare results with the available data for other occurrences in the province, and to build a better foundation for petrological studies in progress concerning the genesis and evolution of the Morro Redondo Complex, as well as the Graciosa Province as a whole.

2. GENERAL GEOLOGY

The A-type Graciosa Province was formed during an extensional (post-collisional *sensu* Liégeois 1998) tectonic period related to the Gondwana amalgamation in S-SE Brazil, during the final stages of the Brasiliano/Pan-African Orogeny, at ca. 580 – 583 Ma (Vlach et al. 2011). It is

composed of several granitic and syenitic plutons from both alkaline and aluminous petrographic associations as well as minor occurrences of K-rich dioritic and bimodal volcanic rocks. They are disposed along an arc parallel to the Atlantic Coast between southeast São Paulo and northwest Santa Catarina states (Fig. 1a), being intrusive into Archean and Neoproterozoic rocks of the Luiz Alves Microplate (Craton) and the Curitiba Microplate and Paranaguá Terrain, respectively (Basei et al. 1992, Siga Jr. et al. 1995). Previous studies on the geology, petrography, mineralogy and geochemistry of the province are found in Gualda and Vlach (2007a, 2007b, 2007c), Vlach and Gualda (2007) and references therein.

Figure 1: Geological context of the Morro Redondo Complex. **(a)** Geological sketch of the Neoproterozoic A-type Graciosa Province (I) and the Morro Redondo Complex (1), as well as contemporaneous volcanosedimentary basins (II) in Southern Brazil and the positioning in the South America Continent (RJ = Rio de Janeiro, BA = Buenos Aires, Argentina). The main regional tectonic units are: A – Ribeira Fold Belt, B – Curitiba Microplate, C – Luiz Alves Microplate (Craton), D – Paranaguá Terrain (Coastal Granitoid Belt). Adapted from Prazeres Filho et al. (2003) and Gualda and Vlach (2007a). **(b)** Geological map of the Morro Redondo Complex and surrounding areas. (1) alluvial-colluvial deposits, (2) contemporaneous bimodal volcanic rocks, (3 to 6) peralkaline alkali-feldspar granites from the **Papanduva Pluton**: (3) protomylonitic facies, (4) cataclastic facies, (5) massive facies, (6) microgranitic facies; (7) peraluminous biotite sienogranites from the **Quiriri Pluton**, (8) Estrela high-K calc-alkaline granite and (9) metasedimentary rocks of the Paranaguá Terrain; (10) gneiss, granulites and migmatites of the Luiz Alves Microplate. Adapted from Vilalva (2007).

2.1. THE MORRO REDONDO COMPLEX

Since the pioneering works by Maack (1953) and Trein (1967) introducing the term “Morro Redondo Granite” in the literature, several authors had contributed to the geology, structure, petrography, geochemistry and geochronology knowledge of its constituting granitic and volcanic rocks (e.g., Kaul 1984, 1997, Machado et al. 1993, Góis 1995, Kaul and Cordani 1994, 2000, Siga Jr. et al. 1994). The term Morro Redondo Complex, used in agreement with ISSC (1987, see also Ulbrich et al. 2001), was coined by Góis (1995), taking into account the association of both intrusive and extrusive rocks. Later, Kaul (1997) subdivided the intrusive rocks into two major units, called Papanduva and Quiriri, respectively; the former being constituted by peralkaline, the latter by slightly peraluminous granitic varieties. In this work we encourage the use of the term *pluton* instead *unit*, once these units certainly constitute structurally defined plutonic bodies, related to distinct intrusive events (cf. Ulbrich et al. 2001).

The Morro Redondo Complex extends to 25 km along N20°W and covers an area of about 250 Km² between the cities of Tijucas do Sul and Garuva, States of Paraná and Santa Catarina, respectively, S Brazil (Fig. 1b). It is intrusive into Archean granulites, gneisses and migmatites of the Luiz Alves Microplate. The eastern border of the complex is close to the N15° – 25°W trending Rio Palmital-Serrinha Shear Zone (RPSSZ), the main limit between the Archaean rocks (to the west) and the Neoproterozoic granitoid rocks of the the Paranaguá Domain (to the east; Fig. 1a).

The granitic exposures are characterized by mountains with elevations up to 1600 m, alternating with remains of eroded plateaus, while flatlands with elevations around 700 – 900 m

define the areas dominated by volcanic rocks (Fig. 2). The main outcrops are fairly weathered blocks and boulders and rare expositions in mountain escarpments and waterfalls. Furthermore, these areas are cover by almost intact Atlantic Forest, with the exception of parts close to the W area, where pines are exploited. Thick vegetation cover, rugged terrain and also the very humid weather strongly limits access to the area and sampling of fresh rocks, especially in the inner portions of the complex.

Figure 2: SRTM 3D digital model for the Morro Redondo Complex area created based on contour lines equidistant at 5 meters through mathematical interpolation using the software Global Mapper. P: Papanduva Pluton, Q: Quiriri Plutons, V: main outcrop area of the associated bimodal volcanic rocks, LA: Luiz Alves Microplate, E: Estrela high-K calc-alkaline granite (Paranaguá Terrain).

2.1.1. Granitic rocks

Papanduva Pluton

The Papanduva Pluton crops out in the northern part of the complex, covering an area about 60 km². It is made of leucocratic ($2 \leq M' \leq 9$) peralkaline granites with whitish to grayish colors. Four main petrographic facies are recognized and mapped (Vilalva 2007, see also Fig. 1b), as follows.

A *massive facies* is made of slightly inequigranular, coarse- to medium-grained massive alkali-feldspar granites, with both sodic-calcic and sodic amphibole and pyroxene (Fig. 3a). It is the main facies of the pluton and crops out in the central and SW pluton areas. Centimetric to metric amphibole-bearing pegmatite veins, as well as miarolitic cavities and vugs appear occasionally and centimetric astrophillyte-bearing microgranular mafic enclaves are rare. A *protomylonitic facies* (Fig.

3b) presents intense late- to post-magmatic deformational structures trending about N30°W/80°SW and N15°E/70°SE. The granites are porphyroclastic, protomylonitic or mylonitic, with porphyroclasts of sodic amphibole (up to 0.5 cm), alkali-feldspar and some quartz, in a saccharoidal fine-grained matrix, which often display whitish to yellowish rare minerals. Microles and vugs are locally seen. A *cataclastic facies* (Fig. 3c) shows slightly deformed coarse- to medium-grained alkali-feldspar granites with darker colors and well developed prismatic pyroxene as the main mafic phase. It crops out only at the northern most portion of the pluton. To end, a *microgranitic facies* (Fig. 3d) is made of slightly inequigranular fine-grained alkali-feldspar microgranites sometimes with planar flow structures defined by amphibole idiomorphic crystals. They appear as centimetric to decametric dikes and other minor bodies which intrude the main granites of both the Papanduva and Quiriri plutons.

Quiriri Pluton

The largest Quiriri Pluton crops out in the central and south portions of the complex and covers an area about 190 km² (Fig. 1b). It is relatively homogeneous and composed of biotite granites ($2 \leq M' \leq 9$) showing grayish to reddish colors, with well-developed quartz crystals. Distinct textural varieties were identified, but they could not be adequately mapped due to outcrops quality and access difficulties. The main facies, here named *Q1*, occurs in the central and southern areas. It has a massive structure and an inequigranular, medium-grained texture showing reddish colors (Fig. 4a). Alkali feldspar constitutes bigger red stained tabular crystals and dominates over whitish tabular plagioclase. Incipient magmatic flow structures and rapakivi-like textures are occasionally seen. A similar variety *Q2*, with a typical grayish color (Fig. 4b), locally amphibole-bearing, appears to NW, while a third, relatively plagioclase-poor facies, with heavy reddish colors crops out in the central and northeastern restricted areas. In the latter, named *Q3*, primary biotite was almost completely replaced by chlorite and other hydrothermal minerals (Fig. 4c). Minor bodies and dikes of granite-porphyrries with alkali-feldspar, plagioclase and quartz phenocrysts (up to 1.2 cm, cf. Fig. 4d) in a fine-grained matrix appear in some outcrops in the northwestern and northeastern areas. These are identified as *Q4* facies.

Granophiric intergrowths may be seen with hand glasses in some varieties of the Q3 and Q4 facies, and miarolitic cavities and vugs are ubiquitous. Simple pegmatite pods, aplite veins as well as microgranular enclaves and both mafic and felsic *schlieren*-like structures are most typical of the main Q1 facies. The enclaves include, besides the typical felsic- and mafic- fine-grained types with granitic (Fig. 4e) and dioritic compositions, respectively, medium- to fine-grained leucocratic enclaves with plagioclase and interstitial mafic minerals similar to those occurring in the granite host (Fig. 4f).

2.1.2. Volcanic and subvolcanic rocks

Volcanic rocks crop out close to the NW border and central areas of the complex, covering an area about 40 km² (Figs. 1b and 2).

General geological and petrographical data were presented by Góis (1995) and Kaul (1997). The main volcanics are porphyritic and microporphyritic rhyolites and alkali-feldspar rhyolites, sometimes showing well developed flow structures. They are peralkaline, with Na-Ca and Na-clinopyroxenes and amphiboles. An alkali-feldspar rhyolite with enigmatite as flow-oriented microphenocrysts crops out in the NWW area. Thin basaltic flows occur between the rhyolite layers. They are made of plagioclase (andesine-labradorite), augite, pigeonite (sometimes as cores in augite), apatite, magnetite and ilmenite and show intergranular to subophitic textures. Interstitial microgranophyric intergrowths do occur and pyroxenes may be substituted by chlorite, biotite, and Ca-amphibole. Afanitic or fine-grained andesites and andesi-basalts with plagioclase (oligoclase-andesine), augite, biotite, magnetite, ilmenite and some quartz are rare.

Basic dikes, with centimetric to metric thicknesses, cross cut the Quiriri granites. Most of them belong to the young Mesozoic (NW-SE and NE-SW) dyke swarms of the Paraná Triple Junction (Coutinho 2008). Some others appear to be sin-plutonic dikes cutting granites, but the observed field relations are poor and almost inconclusive.

2.1.3. Cross-cutting relationships and sequence of the magmatic events

Structural relations among the studied rock are rarely seen in the field and so, the stratigraphy of the magmatic events is still not clear. A rhyolite xenolith was observed in the main

peralkaline granite in the Papanduva Pluton, and the peralkaline microgranitic dikes related to this pluton cut the main biotite granite from the Quiriri Pluton. These observations suggest that the main volcanism preceded to some extent the emplacement of the main peralkaline granite, while at least some peralkaline rocks were emplaced later than the main biotite granites. It must be emphasizing however that the building of a pluton may be very complex, involving the emplacement of several batches of magmas with contrasted rheological properties, so the available information is not enough to draw a desirable scenario.

Figure 3: Petrographic features of the Papanduva Pluton. (a) Macroscopic aspect of hololeucocratic alkali-feldspar granite of the massive facies. The medium-grained equigranular texture is defined by alkali feldspar (Afs), quartz (Qz) and sodic-calcic amphibole (Amp) as the main mafic phase. (b) Macroscopic aspect of alkali-feldspar granite of the protomylonitic facies, with elongated and rounded sodic amphibole porphyroclasts (Amp) in a fine-grained matrix made of quartz (Qz) and potassic feldspar (Kfs). (c) Macroscopic aspect of alkali feldspar granite of the cataclastic facies. The medium-grained equigranular texture is characterized by deformed quartz (Qz) and alkali feldspar (Afs) crystals and interstitial aegirine (Aeg) and sodic amphibole (Amp). (d) Macroscopic aspect of leucocratic alkali feldspar microgranite of the microgranitic facies, with magmatic flow texture defined by oriented prismatic sodic amphibole crystals (Amp) among alkali feldspar (Afs) and quartz (Qz).

Figure 4: Petrographic aspects of the Quiriri Pluton. (a) Massive, medium-grained, hololeucocratic, red-colored syenogranite of the facies Q1, showing equi- to inequigranular texture defined by quartz (Qz), plagioclase (Pl) and red-clouded alkali feldspar crystals (Afs), as well as biotite (Bt) as the main mafic phase. (b) Massive, medium-grained, hololeucocratic, grayish syenogranite of facies Q2. The inequigranular texture is defined by red-grayish alkali feldspar (Afs), minor plagioclase (Pl) and quartz (Qz) crystals and interstitial biotite (Bt). (c) Massive, medium- to coarse grained, plagioclase-poor, hololeucocratic, red-colored syenogranite of facies Q3. Large red-clouded alkali feldspar crystals (Afs) and minor quartz (Qz), plagioclase (Pl) and chlorite (Chl) pseudomorphs after biotite define an inequigranular texture. (d) Porphyritic syenogranite of facies Q4 showing tabular alkali feldspar (Afs) and globular quartz megacrysts (Qz) in a fine-grained matrix of poikilitic quartz enclosing plagioclase, chlorite (Chl) pseudomorphs after biotite and some late alkali feldspar crystals. (e) Detail of microgranular felsic enclave (right) composed of quartz, feldspars and chlorite pseudomorphs after biotite. Note euhedral plagioclase (Pl) and alkali feldspar (Afs) megacrysts that may represent

Figure 4 (cont): xenocrysts from the syenogranite of facies Q1 (left) containing alkali feldspar (Afs), quartz (Qz), plagioclase (Pl) and biotite (Bt) in a inequigranular texture. (f) Detail of leucocratic enclave containing mainly plagioclase and interstitial chlorite and epidote (dark colors) replacing primary biotite, within the inequigranular, red colored inequigranular syenogranite of facies Q1 showing alkali feldspar (Afs), plagioclase(Pl), quartz (Qz) and interstitial biotite (Bt).

3. ANALYTICAL METHODS

In this work, besides conventional field and petrographic data, we present magnetic susceptibility (MS), mineral and whole-rock chemical data obtained for the intrusive rocks at the laboratories of the Instituto de Geociências, Universidade de São Paulo.

The MS measurements were made with the GM Instruments Portable Susceptibilimeter SM-20. A mean of 10 measurements per sample were taken in appropriate outcrops during the field work and in rock slabs made later.

Chemical mineral compositions were obtained using WDS microanalysis with the JEOL JXA-8600S EPMA under 15 kV and 20 nA for the column acceleration voltage and beam current. Pyroxenes, amphiboles, biotite, alkali feldspar and plagioclase were analysed following the procedures described by Gualda and Vlach (2007b). Matrix corrections and data reduction were made with the PROZA software (e.g. Bastin and Heijligers 1990). Mineral formulae and estimates of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios were made using the Mincal software (GAR Gualda and SRF Vlach, unpublished, see also Deer et al. 1992 and Droop 1987). Amphiboles were classified according to Leake et al. (1997, 2004); Fe^{2+} and Fe^{3+} were estimated following a variant of the method proposed by Schumacher (1997), as discussed in Gualda and Vlach (2005). Clinopyroxene nomenclature follows Morimoto et al. (1988).

Whole-rock chemical analyses were made in the ICP-AES/MS and XRF Laboratories. Major-, minor- and some trace-elements were quantified by ICP-AES and XRF respectively, while mostly trace-elements were measured by ICP-MS, following methods described by Mori et al. (1999) and Navarro et al. (2008), respectively. Radiogenic heat production per volume (A) was calculated using Th and U contents measured with ICP-MS, following Rybach (1988):

$$A (\mu\text{Wm}^{-3}) = 10^{-2} \cdot \rho \cdot [3.48 \cdot \text{K}_2\text{O} + 2.56 \cdot \text{Th} + 9.52 \cdot \text{U}]$$

where K₂O is given in wt. % and Th and U in ppm. A medium rock density (ρ) of 2.70 g/cm³ was chosen.

4. RESULTS

4.1. PETROGRAPHY

Representative quantitative modal data for the granitic rocks are presented in Fig. 5. The Papanduva and Quiriri plutons are made of *hypersolvus* alkali-feldspar granites and *subsolvus* syeno-granites, respectively. A felsic microgranular enclave from the Quiriri Pluton plots as a monzogranite. Brief petrographic descriptions of these rocks are given in the following; additional micro-structural relationships among the main rock-forming minerals will be presented in the mineralogical section.

Figure 5: Modal Quartz (Q) - Alkali Feldspar (F) - Plagioclase (P) diagram for oversaturated plutonic rocks according to Streckeisen (1976) showing compositional variations registered for Papanduva and Quiriri Plutons of the Morro Redondo Complex. Labeled fields are: (1) alkali-feldspar granite; (2) syenogranite and (3) monzogranite.

4.1.1. Papanduva Pluton

The texture of the main massive facies is given by large tabular crystals of mesoperthitic alkali feldspar with well-developed quartz; amphiboles and pyroxene are interstitial and homogeneously distributed (Fig. 6a). Two contrasted amphibole generations are seen: a green Na-Ca amphibole is relatively earlier in the crystallization sequence and corresponds to the main mafic

phase, while a blue Na-amphibole appears as interstitial isolated crystals and late overgrowths. Late zoned Na-clinopyroxene appears as interstitial isolated idiomorphic crystals, fibro-radiated mineral aggregates, as well as ubiquitous mantles over amphibole. Zircon, chevkinite, fluorite, astrophyllite and some ilmenite, magnetite and titanite are the main accessory phases.

The rare microgranular mafic enclaves are marked by euhedral to subhedral quartz and alkali feldspar megacrysts in a fine-grained, hypidiomorphic to xenomorphic quartz-feldspathic matrix with Ca-amphibole, apatite and astrophyllite.

Deformational textures, developed in varying degrees, characterize the protomylonitic and cataclastic facies in this pluton. In the former, textures are defined by compositionally zoned Na-amphibole, perthitic alkali feldspar and some quartz porphyroclasts (2.0 – 4.0 mm) in a fine-grained matrix made of recrystallized quartz, slightly perthitic microcline and albite, joined by Na-clinopyroxene and the accessory minerals (Fig. 6b). In the cataclastic facies, interstitial and deformed Na-clinopyroxene and amphibole crystals, quartz surrounded by moats of fine recrystallized grains, crystal microfractures filled in by late magmatic minerals and kinked mesophertitic alkali feldspar crystals are common features (Fig. 6c). Fluorite, astrophyllite, titanite, aenigmatite and some ilmenite are accessory minerals common to both facies. Zircon and late magnetite appear only in the cataclastic facies, while a variety of late- to post-magmatic “agpaitic” Ti-, Zr-, and REE-bearing rare silicates and oxides, such as narsarsukite, neptunite, elpidite and other (Na, K) zirconosilicates, britholite, turkestanite, nacareniobsite and brookite, as well as some still unidentified minerals, occurs only in the protomylonitic facies, regularly distributed or filling in vugs and miarolitic cavities in the host rock (Vilalva and Vlach 2006, 2010, Vlach and Vilalva 2007).

The microgranites are equi- to inequigranular fine-grained rocks with magmatic flow structures marked by Na-amphibole. They are characterized by abundant micro-graphic intergrowths with varying morphologies (Fig. 6d). The mafic minerals are Na-amphibole and/or Na-clinopyroxene, while chevkinite, fluorite (?), post-magmatic ilmenite and zircon are the main accessory minerals.

4.1.2. Quiriri Pluton

The granite varieties from the Quiriri Pluton present variable quantities of perthitic alkali feldspar, quartz and sodic plagioclase (oligoclase) with allanite, titanite, fluorite, zircon, apatite, magnetite and ilmenite as the main accessories. The most typical Q1, and also the Q2 facies, present equi- to inequigranular hypidiomorphic textures defined by somewhat larger tabular crystals of alkali feldspar, variable deformed quartz (undulose extinction, deformation lamellae), plagioclase, and interstitial biotite (Figs. 7a, b). Hornblende is occasional in the grayish variety. The main textural contrasted types are alkali-feldspar granites of the Q3 facies, with abundant granophyric intergrowths in the matrix (Fig. 7c) and porphyritic syenogranites (granite porphyries) of the Q4 facies with perthitic alkali-feldspar, some sodic plagioclase, and quartz megacrysts in a fine-grained quartz-feldspathic matrix containing biotite, zircon, magnetite, ilmenite, apatite and allanite (Fig. 7d).

Hydrothermal alteration is ubiquitous in all petrographic facies but the grayish Q2 (Fig. 4). Related textures include biotite crystals replaced by chlorite + epidote + magnetite, post-magmatic albite interstitial to alkali-feldspar or as partial rims over plagioclase, sericitic or saussuritic plagioclase and sericitic and red-clouding of alkali feldspar (e.g. Figs. 4c, d). The red-clouding phenomenon in feldspars is mostly a product of fluid–rock interaction due to the precipitation of rosettes and needles of hematite from hydrothermal fluids into micro pores in the alkali feldspar surface, resulting of sub-solidus mineral–fluid replacement processes (e.g. Putnis et al. 2007). In many outcrops, the granite boulders show the red-staining concentrated in specific areas, which are always associated with epidote-filled microfractures.

The typical microgranular felsic enclaves are monzogranites with quartz, feldspars and chlorite pseudomorphs after biotite. Euhedral alkali feldspar, rounded quartz and some plagioclase megacrysts, arguably xenocrysts from the host granite, are common (Fig. 7e). The mafic microgranular enclaves are quartz-monzodiorites with biotite as the main mafic mineral, together with apatite, magnetite, and ilmenite. The leucocratic microgranular enclaves are made mainly of euhedral tabular plagioclase (andesine), up to 80% volume. Interstitial chlorite, epidote, fluorite, titanite and magnetite have totally replaced the primary biotite and, perhaps, amphibole (Fig. 7f).

Figure 6: Microtextural features of the Papanduva Pluton. **(a)** Textural aspect of alkali feldspar granite of the massive facies showing equi- to inequigranular texture with tabular mesoperthitic alkali feldspar crystals (Afs), sometimes with albitic rims (Ab), as well as quartz (Qz) and interstitial richterite (Rct) crystals. **(b)** Textural aspect of alkali-feldspar granite of the protomylonitic facies, with potassic feldspar (Kfs) and arfvedsonite (Arf) porphyroclasts, the latter mantled by aegirine (Aeg), in a fine-grained recrystallized matrix of quartz (Qz), post-magmatic albite and potassic feldspar (Kfs). **(c)** Textural aspect of alkali feldspar granite of the cataclastic facies, with subhedral, perthitic to mesoperthitic alkali feldspar (Afs), quartz with undulose extinction (Qz) and interstitial aggregates of aegirine (Aeg), as well as some riebeckite (Rbk). Note recrystallized fine-grained quartz filling in fractures in feldspar (arrows).

Figure 6 (cont.): (d) Textural aspect of alkali-feldspar microgranite of the microgranitic facies with equi- to inequigranular texture defined by tabular alkali feldspar crystals (Afs) with interstitial quartz (Qz), aegirine (Aeg) and arfvedsonite (Arf). Graphic intergrowths between quartz and alkali feldspar are common (arrows). Photomicrographs obtained with crossed polarizers.

Figure 7: Microtextural features of the Quiriri Pluton. **(a)** Textural aspect of massive, medium-grained inequigranular syenogranite of facies Q1 with slightly larger perthitic alkali feldspar crystals (Afs) and minor plagioclase (Pl), quartz (Qz) and interstitial biotite (Bt) crystals. **(b)** Textural aspect of massive, fine- to medium-grained syenogranite of facies Q2 showing equi- to inequigranular texture made of slightly larger alkali feldspar (Afs) and quartz (Qz) crystals, minor saussuritic plagioclase (Pl) and interstitial euhedral biotite. **(c)** Textural aspect of massive, medium grained, plagioclase-poor syenogranite of facies Q3 with a inequigranular texture defined by alkali feldspar crystals (Afs) in granophyric intergrowths with quartz (Qz), scarce plagioclase (Pl) and interstitial chlorite (Chl) pseudomorphs after biotite. **(d)** Textural aspect of porphyritic syenogranite (granite porphyry) of facies Q4 with sericitic and red-clouded alkali feldspar (Afs) and globular quartz (Qz) megacrystals in a fine-grained quartz-feldspatic matrix with chlorite (Chl) pseudomorphs after biotite. **(e)** Textural detail of microgranular monzogranitic enclave within syenogranite of facies Q1 showing euhedral alkali feldspar (Afs) and globular quartz (Qz) megacrystals (xenocrystals ?) in a fine-grained matrix of poikilitic quartz (Qz),

Figure 7 (cont.): minor plagioclase, some alkali feldspar and chlorite (Chl) pseudomorphs after biotite. **(f)** Detail of leucocratic enclave within syenogranite of Q1 facies, essentially made of euhedral plagioclase crystals (Pl), as well as chlorite (Chl) and epidote (ep) pseudomorphs after biotite and/or amphibole. Photomicrographs obtained with crossed polarizers.

5. MAGNETIC SUSCEPTIBILITIES

Magnetic susceptibility measurement results are displayed as histograms in Fig. 8. Most values obtained for samples from the Papanduva Pluton are lower than 1.0×10^{-3} SI, with a mean and mode values of 0.42×10^{-3} and 0.1×10^{-3} SI (Fig. 8a). Exceptions are some samples from the *cataclastic facies*, which result in values as high as 6.0×10^{-3} SI, due to the presence of almost pure post-magmatic magnetite in micro-fractures or over Na- amphibole and pyroxene. In the case of the Quiriri Pluton, albeit for some measurements down to 0.04×10^{-3} SI, obtained for samples from the grayish Q2 facies, the mean and mode are 2.57×10^{-3} and 2.3×10^{-3} SI (Fig. 8b), up to 5-fold higher than the values obtained for the Papanduva samples as expected from their modal primary magnetite content.

The MS of the peralkaline rocks from the Papanduva Pluton are among the lowest observed for alkali-feldspar granites and syenites from the alkaline association in the Graciosa Province, with typical values around 1.0×10^{-3} SI. The values observed Quiriri samples, as well their variation range, are very similar to those measured in the aluminous association elsewhere in the province (cf. Gualda and Vlach 2007a).

Figure 8: Histograms (absolute frequency) showing the magnetic susceptibility (MS) variation for representative samples of the Papanduva (a) and Quiriri (b) Plutons.

6. MINERALOGY

General micro-structural and chemistry of the main granite-forming minerals are presented in the following. Representative chemical compositions of feldspars, amphiboles, clinopyroxenes and biotite are presented in Table I.

6.1. ALKALI FELDSPAR

Alkali feldspar from the Papanduva Pluton forms mesoperthitic, euhedral to subhedral crystals in massive granitic and microgranitic facies and slightly perthitic porphyroclasts as well as granoblastic microcline in the protomylonitic and cataclastic facies. Their integrated compositions, which should approach primary compositions, vary between $\text{Ab}_{35-66}\text{An}_{0-1}\text{Or}_{65-34}$ and $\text{Ab}_{2-15}\text{An}_0\text{Or}_{99-85}$, respectively (Fig. 9). They are somewhat Fe^{3+} -richer when compared with alkali feldspars from peralkaline rocks of the Serra da Graciosa region within the province (Gualda and Vlach 2007b). Late- to post-magmatic albite is observed also as interstitial limpid crystals or as swapped-rims over alkali-feldspars in most samples. In the protomylonitic and cataclastic facies, besides granoblastic in the rock matrix, albite also appears as euhedral laths forming intergrowths with mafic minerals, which resemble the *khybinitic* texture observed in some undersaturated alkaline rocks (e.g. Gerasimovsky et al. 1974). Compositions are close to the ideal end-member ($\text{Ab}_{99-100}\text{An}_{0-0.1}\text{Or}_{1-0}$, cf. Table I, Fig. 9). It is worth to note these albite laths are slightly richer in Fe^{3+} (up to 1.7 wt. % Fe_2O_3) than the most typically post-magmatic albite crystals (up to 1.3 wt. % Fe_2O_3).

The alkali-feldspar from the Quiriri samples appears as perthitic, euhedral to subhedral crystals, with better developed chessboard textures. Their compositions are similar to those observed in other plutons of the aluminous association inside the Graciosa Province (Gualda and Vlach 2007b), ranging $\text{Ab}_{26-41}\text{An}_{0-1}\text{Or}_{74-58}$ (Table I, Fig. 9). As expected from the *subsolvus* character of these rocks, the integrated alkali-feldspar compositions are Or-rich when compared with those of the Papanduva samples. Almost pure albite is also seen interstitially to crystals of alkali-feldspar and as partial rims on sodic plagioclase in plagioclase-alkali feldspar contacts.

Figure 9: Average compositions of core, intermediate zone and rim for alkali feldspar and albite, and individual chemical analysis of plagioclase in the An-Ab-Or molecular ternary plot for representative samples of the Quiriri (a) and Papanduva (b) Plutons. Available chemical data for feldspars from other plutons of the Graciosa Province are shown for comparison (c): plutons of the alkaline (1) and aluminous (2) associations in the Serra da Graciosa region (Gualda and Vlach 2007b). Solvus curves for $P_{total} = 1$ kbar, according to the model after Fuhrman and Lindsley (1988). Small triangles in (a) and (c) show compositions of coexistent plagioclase and alkali feldspar crystals. Symbols as in Fig. 5. Discussion in the text.

6.2. Plagioclase

Sodic primary plagioclase occurs in the Quiriri Pluton as isolated euhedral to subhedral tabular crystals, sometimes in aggregates of 2 to 4 grains, often with post-magmatic partial albite rims. Sericitic or saussuritic alterations are observed in varying degrees in most samples. Their compositions correspond to oligoclase, $Ab_{73-87}An_{24-11}Or_{2-8}$. Compositional zoning is normal, with relatively Ca-rich cores, to slightly oscillatory (Table I, Fig. 9). Optical data obtained for plagioclase from both the felsic microgranular and the leucocratic medium- to fine-grained enclaves indicate somewhat more calcic compositions, up to sodic-andesine (An_{30-35}).

6.3. Amphiboles

Sodic-calcic and sodic amphiboles are the main mafic phases in the Papanduva peralkaline granites. They appear as isolated interstitial crystals, in aggregates of 3-4 grains or as elongated

porphyroclasts in the most deformed samples of the protomylonitic facies. Most crystal displays concentric to irregular patchy compositional zoning. Na-Ca amphibole (Fe-richterite) is found only in the massive facies, while sodic varieties are ubiquitous and correspond both to arfvedsonite and riebeckite, the latter being more typical in the cataclastic and microgranitic facies. The observed main compositional variations are defined by increasing Si, Fe^{3+} , Na and K contents and decreasing Al, Fe^{2+} and Ca contents from core to crystal rims. These variations do not span a large compositional range as observed in other similar plutons of the Graciosa Province however, since Ca-richer compositions are lacking (Table I, Fig. 10a).

Ca-amphiboles occur only in samples from the grayish Q2 facies of the Quiriri Pluton. They form rare isolated euhedral crystals partially replaced by chlorite, epidote, magnetite and fluorite. In some samples only pseudomorphosed crystals are seen. Compositions correspond to ferro-hornblende, edenite, and ferro-edenite, with Na contents (up to 2.4 wt. % Na_2O) higher than those registered in similar plutons from the province (Gualda and Vlach 2007c). Zoning is very discrete, with some increasing in Na and K and decreasing in Ca and Al contents towards crystal rims (Table I, Fig. 10a).

Table I: Typical WDS analyses (wt. %) for alkali feldspar, albite, plagioclase, amphiboles, clinopyroxenes and biotite of the granites from Papanduva and Quiriri plutons, Morro Redondo Complex. Analysis of alkali feldspar from sample MR-19B refers to integrated perthitic or meso-perthitic compositions. b.d.l. = below detection limit, (-) = not analysed.

Mineral	Alkali Feldspar				Albite		Plagioclase		Fe-richterite	Arfvedsonite	Riebeckite	Aegirine-Augite		Aegirine		Biotite	
Sample	MR-39	MR-02A	MR-19B	MR-201B	MR-01A	MR-61	MR-19B	MR-201B	MR-39	MR-50(2)	MR-11 (A)	MR-121	MR-41	MR-06	MR-186A	MR-193	
Pluton	Papanduva		Quiriri		Papanduva		Quiriri		Papanduva			Papanduva			Quiriri		
Facies	massive	protomylon.	Q2	enclave	protomylon.		Q2	enclave	massive	protomylon.	cataclastic	massive	protomylon.			Q2	
Cristal	1	1	1	4	1	2	1	7	5	1	1	1	1	6	1	1	
Point	1, n	1, n	1, n	2, i	1, n	2, b	3, n	2, i	2, i/n	1, b	1, b	1, b	4, n	1, b	1-n	1-b	
SiO ₂	66.53	64.55	64.96	64.83	68.94	68.91	63.71	61.95	47.5	49.9	50.2	51.07	52.57	51.48	35.80	36.08	
TiO ₂	b.d.l.	b.d.l.	0.03	b.d.l.	b.d.l.	0.12	b.d.l.	0.01	1.59	0.30	0.91	2.12	6.47	1.35	3.96	3.55	
ZrO ₂	-	-	-	-	-	-	-	-	0.08	b.d.l.	0.03	1.27	0.09	0.04	-	-	
Al ₂ O ₃	18.58	18.25	18.37	18.95	18.51	18.95	22.55	23.37	1.91	0.16	0.49	0.23	0.21	0.30	12.49	13.11	
FeO _T	0.43	0.23	0.03	0.08	1.45	0.94	0.11	0.26	32.6	33.2	34.8	27.49	24.94	27.80	25.40	25.97	
MnO	b.d.l.	0.02	b.d.l.	0.02	b.d.l.	b.d.l.	0.06	0.00	0.74	0.80	0.57	0.29	0.28	0.94	0.29	0.42	
ZnO	-	-	-	-	-	-	-	-	0.21	0.41	0.28	0.13	0.08	0.31	0.05	0.00	
MgO	-	-	-	b.d.l.	-	-	-	b.d.l.	0.69	0.05	0.33	0.13	b.d.l.	0.05	7.53	6.87	
CaO	b.d.l.	b.d.l.	0.04	0.18			4.16	4.79	4.45	0.01	0.33	4.80	0.46	0.29	0.03	0.03	
BaO	b.d.l.	b.d.l.	0.38	0.22	-	b.d.l.	-	b.d.l.	-	-	-	-	-	-	0.15	0.08	
SrO	b.d.l.	b.d.l.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Na ₂ O	4.92	0.21	3.22	4.66	10.55	11.84	8.04	8.59	5.46	7.65	6.64	10.35	12.77	13.04	0.10	0.07	
K ₂ O	9.70	16.79	11.85	10.08	0.07	0.05	0.60	0.91	1.43	3.76	1.81	b.d.l.	b.d.l.	b.d.l.	9.11	9.55	
F	-	-	-	-	-	-	-	-	0.50	0.92	0.37	-	-	-	0.63	0.73	
Cl	-	-	-	-	-	-	-	-	0.03	b.d.l.	b.d.l.	-	-	-	0.33	0.36	
H ₂ O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.57	3.57	
Sum	100.15	100.05	98.88	99.04	99.70	100.96	99.23	99.905	96.89	97.39	96.79	97.87	97.88	95.59	99.43	100.39	
O=F=Cl	-	-	-	-	-	-	-	-	0.22	0.39	0.16	-	-	-	0.96	1.10

Figure 10: Compositional variation diagrams for the main mafic minerals in the Papanduva and Quiriri Plutons, Morro Redondo Complex. (a) $(\text{Si} + \text{Na} + \text{K})$ vs. $(\text{Ca} + \text{IVAl})$ cationic plots showing the compositional evolution of amphiboles from the Morro Redondo Complex (i). In (ii) and (iii) compositional trends registered for other plutons of the Graciosa Province are portrayed for comparison: 1, Serra da Graciosa Plutons, alkaline association (Gualda and Vlach 2007b, 2007c); 2, Serra da Graciosa Plutons, aluminous association (Gualda and Vlach 2007b, 2007c); 3, Mandira Pluton, alkaline association (Santos and Vlach 2010); 4, Mandira Pluton, aluminous association (Santos and Vlach 2010); 5, Corupá Pluton, alkaline association (Garin 2003). The nomenclature of ideal amphibole end-members are shown in (iv). End-members with the A position completely vacant fall along the lower line, end-members with the A position completely filled fall along the upper line. (b) $\text{Na-Mg-(Fe}^{2+} + \text{Mn)}$ cationic plots showing the compositions of clinopyroxenes in the Papanduva Pluton (i). In (ii) compositional trends observed in other plutons from the alkaline association in the Graciosa Province are shown: 1, Corupá Pluton (Garin 2003); 2, Serra da Graciosa Plutons (Gualda and Vlach 2007b). (c) $\text{IVAl vs. Fe}/(\text{Fe} + \text{Mg})$ cationic plots for biotite of Quiriri Pluton (i). In (ii) compositional trends for other aluminous occurrences from the Graciosa Province are drawn for comparison: 1, Serra da Graciosa Plutons (Gualda and Vlach 2007b); 2, Mandira Pluton (Santos and Vlach 2010); 3, Guaraú Pluton (R. P. Garcia and S. R. F. Vlach unpublished data). Symbols as in Fig. 5.

6.4. CLINOPYROXENES

Clinopyroxenes appear in samples of the Papanduva Pluton mainly as interstitial yellow-greenish isolated crystals or in aggregates of several grains and fibrous aggregates. They comprise both late- and post-magmatic phases and often appear as mantles over amphiboles. Concentric, sector and irregular compositional zoning are common features in all samples. Some samples from the massive and protomylonitic facies present two other textural generations of pyroxene, recognized by their contrasted pleochroic schemes, one with dark-green, other with orange to yellow pleochroic colors. The former is replaced by a yellow-greenish clinopyroxene and the latter appears as mantles over both phases in the protomylonitic facies.

The widespread yellow-greenish clinopyroxene corresponds to an aegirine or titanian aegirine ($\text{Eg}_{81-99}\text{Jd}_{5-0}\text{WEF}_{15-0}$), with up to 7.0 wt. % TiO_2 . The dark-green variety is an aegirine-augite ($\text{Eg}_{72-80}\text{Jd}_1\text{WEF}_{27-18}$) and the orange-yellowish phase corresponds to an almost pure aegirine ($\text{Eg}_{93-97}\text{Jd}_{3-1}\text{WEF}_{5-2}$) with relatively high Mn contents (up to 0.97 wt. % MnO, cf. Table I). The main compositional trend is defined by an increasing in Na and Fe^{3+} and decreasing in Ca and Fe^{2+} contents from crystals cores to rims, over a relatively narrow range. The compositions plot along the Na (Eg) – $\text{Fe}^{2+}+\text{Mn}$ (Hd) axis in the ternary plot Na (Eg) x Mg (Di) x $\text{Fe}^{2+}+\text{Mn}$ (Hd) presented in Fig. 10b, with most compositions close to the Eg apex, a compositional trait that highly contrasts with the observed evolutionary trends in the whole Graciosa Province, marked by an initial Mg decreasing and $\text{Fe}^{2+} + \text{Mn}$ increasing, before a moderate increase in the Na contents (Fig. 10b). Thus, the clinopyroxenes from the Papanduva Pluton correspond to the most evolved compositions observed in the province, with high Na (9.7 – 13.6 wt. % Na_2O) and negligible Mg (lower than 0.2 wt. % MgO) contents.

6.5. BIOTITE

Biotite is the characteristic mafic mineral in samples from the Quiriri Pluton. It occurs as interstitial crystals with orange to brownish pleochroism. The compositions observed in the granitic rocks are nearly homogeneous, with $\text{Fe}^t/(\text{Fe}^t+\text{Mg})$ cationic ratios and Al^{IV} varying between 0.56 - 0.70 and 2.1 – 2.5, respectively (Table I, Fig. 10c). The crystals in the mafic microgranular enclaves

are slightly more magnesian, with $\text{Fe}^{II}/(\text{Fe}^{II}+\text{Mg})$ ratios between 0.47 and 0.61. Most compositions plot in the field common to the biotites from anorogenic alkaline suites of Adbel-Rahman (1994). These compositions in part overlap those for biotite in plutons of the Serra da Graciosa Region (Gualda and Vlach 2007b) and are more magnesian than the biotite from the Mandira (Santos and Vlach 2010) and Guaraú Massifs (R.P. Garcia and S.R.F. Vlach unpublished data) from the Graciosa Province (Fig. 10c).

A remarkable compositional feature of biotite from the studied samples, as well as from most occurrences in the province, is that it does not follow the *Fe-avoidance* model of Muñoz (1984), and variable positive correlations are observed between its F and Fe contents. In fact, its X_F and X_{Mg} molar fractions plot in a field for which this model does not play a major role (Mason 1992, Charoy and Raimbault 1994, Vilalva 2010).

7. WHOLE-ROCK GEOCHEMISTRY

Major- and trace-element compositions of representative samples of the granitic rocks of Papanduva and Quiriri plutons, for which a complete FRX and ICP data set are available, are presented in Table II. Additional partial data may be requested from the first author. Moreover, some previous partial data were also presented by Kaul and Cordani (2000) for granites and Góis (1995) for granites and volcanic rocks. In the latter case, an alkaline character for the rhyolites, with both comendites and panterellerites varieties, and a calc-alkaline to alkaline character for basalts, andesi-basalts and andesites, were indicated by the author.

The main major- and trace-element geochemical signatures of the granites from Morro Redondo Complex are typical of A-type or intraplate granites from other occurrences in the Graciosa Province and elsewhere (Collins et al. 1982, Pearce et al. 1984, Pitcher 1993, Whalen et al. 1987, Vlach and Gualda 2007, Frost and Frost 2011). They are alkali-rich ($8.7 \leq \text{Na}_2\text{O} + \text{K}_2\text{O} \leq 9.3$ wt. %), ferroan (Frost et al. 2001, Frost and Frost 2011) evolved rocks that exhibit a narrow compositional range ($74 \leq \text{SiO}_2 \leq 78$ wt. %), plotting close to the granitic minimum at relatively low pressures in the normative Or-Ab-Qz diagram (Fig. 11); in which the relatively Qz-poor and Or-rich

nature of the aluminous samples from the Quiriri Pluton are well depicted. Selected geochemical diagrams are shown in Fig. 12 to emphasize the main contrasts between the alkaline and aluminous (subalkaline) granites. The fe# numbers are ≥ 0.96 and between 0.87 and 0.91, while the molecular ASI (Alumina Saturation) and AI (Algaipitic) Indexes vary between 0.76 – 0.94, 1.04 – 1.28 and 1.00 – 1.04, 0.88 – 0.91 in the peralkaline granites and in the main peraluminous granites from the Papanduva and Quiriri plutons, respectively. In the former pluton, these indexes show a distinct larger variation range as well as a very good positive correlation. It is note to worth that in the Quiriri Pluton, the hornblende-bearing granite (facies Q2), as well as the felsic enclave hosted in the main granite have lower fe# (0.82 and 0.83, respectively) and AI, while the granite porphyries (facies Q4) present fe# values similar to the peralkaline granites (0.99 – 1.00) as well as a somewhat higher AI. As expected, the peralkaline granites have lower CaO contents, as well as $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ molecular ratios than the main aluminous ones. These ratios correlate positively in the peralkaline samples.

Figure 11: Normative Or-Ab-Qz diagram for selected samples from the Quiriri and Papanduva plutons. Cotectic curves, minima and eutectic points are from Winter (2001). Comments in the text.

Table II: Representative whole-rock chemical data for the granites of Papanduva and Quiriri plutons, Morro Redondo Complex. Oxides and elements are given in wt. % and ppm, respectively. (*) FRX analyses, others ICP-MS analyses. LOI = lost on ignition, fe# = $\text{FeO}^T/(\text{FeO}^T + \text{MgO})$, oxide wt. %; AI (Algaipitic Index) = $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ and ASI (Alumina Saturation Index) = $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ in moles; Tsat(zr) and Tsat(ap) = zircon and apatite saturation temperatures ($^{\circ}\text{C}$, nc = not calculated); A = Radiogenic heat production per volume unit (μWm^{-3}). Discussion in the text.

Sample	MR-215	MR-62	MR 32	MR 39	MR 50(A+)	MR 02	MR 21	MR 01A	MR 01D
Pluton									
Facies	massive				Papanduva protomylon.			cataclastic	microgranitic
SiO ₂	74.53	75.40	76.04	75.91	74.55	75.38	77.78	75.98	73.99
TiO ₂	0.179	0.224	0.137	0.219	0.163	0.161	0.086	0.211	0.109
Al ₂ O ₃	11.30	11.33	10.79	11.52	9.89	10.58	11.25	10.83	11.34
Fe ₂ O ₃ ^T	3.09	2.85	3.65	2.91	5.62	3.85	1.77	2.91	3.75
MnO	0.046	0.051	0.045	0.042	0.084	0.059	0.030	0.060	0.054
MgO	0.05	0.10	0.03	0.07	0.03	0.03	0.02	0.01	0.03
CaO	0.28	0.35	0.21	0.20	0.15	0.23	0.13	0.26	0.26
Na ₂ O	4.58	4.21	4.97	4.14	5.24	4.68	4.22	4.34	4.65
K ₂ O	4.69	4.71	4.08	4.74	3.77	4.33	4.75	4.66	4.69
P ₂ O ₅	0.012	0.015	0.007	0.016	0.007	0.008	0.008	0.009	0.004
LOI	0.20	0.20	0.48	0.50	0.34	0.32	0.22	0.44	0.30
Total	98.96	99.44	100.44	100.27	99.84	99.63	100.26	99.71	99.18
fe#	0.982	0.962	0.991	0.974	0.994	0.991	0.988	0.996	0.991
ASI	0.861	0.895	0.832	0.936	0.762	0.826	0.913	0.856	0.859
Al	1.116	1.061	1.167	1.037	1.284	1.171	1.074	1.125	1.122
Li	38.6	31.8	65.1	30.0	178.6	73.2	24.7	29.7	84.4
Be	7.93	6.57	8.34	5.87	9.40	11.0	6.41	7.90	5.72
Ga*	32	29	32	28	36	33	32	30	38
Zn*	135	114	200	114	347	199	89	147	158
Rb	130	123	151	104	302	195	147	136	132
Sr	11.0	16.0	5.68	5.46	4.77	4.92	1.66	5.22	2.32
Y	170	112	303	71.4	323	165	145	168	59.8
Zr*	776	781	1174	708	2428	1798	748	1217	523
Nb	48.0	45.6	55.8	44.3	88.1	52.4	21.3	65.5	21.5
Cs	9.39	0.76	0.64	0.40	1.25	1.34	0.51	1.61	0.59
Ba	83.7	144	20.9	81.0	16.2	28.5	4.22	40.0	4.57
La	104	188	168	90.3	119	94.1	200	164	31.3
Ce	231	297	237	123	233	177	268	274	63
Pr	24.4	34.6	41.9	18.1	30.1	21.8	32.4	32.5	8.79
Nd	91.1	120	180	63.9	119	82.8	113	120	35.3
Sm	21.1	23.6	51.2	11.9	31.8	20.1	21.7	26.1	8.96
Eu	0.92	1.07	2.14	0.55	1.34	0.80	0.76	1.01	0.32
Gd	21.4	20.6	56.3	10.6	39.1	21.7	20.5	26.2	9.35
Tb	3.63	3.23	8.77	1.76	6.78	3.78	3.05	4.46	1.50
Dy	21.8	18.7	50.0	11.3	43.0	24.3	17.5	28.2	9.27
Ho	4.54	3.78	9.48	2.46	9.19	5.27	3.44	5.93	1.95
Er	12.5	10.6	23.5	7.68	26.1	15.7	9.49	17.1	5.92
Tm	1.81	1.53	2.91	1.20	3.73	2.31	1.31	2.48	0.95
Yb	11.6	10.1	17.9	8.55	24.1	15.4	8.40	15.9	7.37
Lu	1.57	1.41	2.58	1.30	3.46	2.29	1.22	2.21	1.27
Hf	22.1	19.6	31.2	19.8	61.2	46.4	19.4	33.7	13.1
Pb	42.7	24.1	61.5	18.3	88.3	39.5	21.2	50.1	12.6
Th	32.4	26.9	37.9	26.1	47.9	32.4	22.2	42.1	11.4
U	3.70	3.28	4.85	2.89	7.81	6.20	2.01	4.43	1.27
Tsat(zr)	nc	nc	nc	nc	nc	nc	nc	nc	nc
Tsat(ap)	nc	nc	nc	nc	nc	nc	nc	nc	nc
A	3.6	3.1	4.3	3.0	5.7	4.2	2.5	4.5	1.6

Table II: cont.

Sample	MR-161	MR-164	MR-202	MR-178	MR-174	MR-17	MR-201A	MR-193	MR-185	MR-186A	MR-201B
Pluton	Quiriri										
Facies	Q1							Q2			Enclave
SiO ₂	75.74	75.06	75.37	75.37	74.90	74.40	75.06	75.21	75.38	75.41	72.12
TiO ₂	0.178	0.196	0.183	0.178	0.191	0.184	0.201	0.189	0.202	0.193	0.353
Al ₂ O ₃	12.59	12.67	12.54	12.53	12.91	12.63	12.66	12.60	12.44	12.92	13.77
Fe ₂ O ₃ ^T	1.47	1.47	1.37	1.37	1.40	1.39	1.50	1.43	1.51	1.03	2.59
MnO	0.027	0.026	0.021	0.023	0.025	0.025	0.023	0.028	0.033	0.016	0.061
MgO	0.14	0.16	0.15	0.14	0.16	0.16	0.20	0.19	0.16	0.12	0.49
CaO	0.53	0.69	0.66	0.64	0.68	0.62	0.70	0.69	0.63	0.59	1.08
Na ₂ O	3.52	3.43	3.46	3.42	3.44	3.54	3.53	3.46	3.46	3.47	3.85
K ₂ O	5.10	5.13	5.15	5.15	5.27	5.20	5.16	5.15	5.11	5.27	4.91
P ₂ O ₅	0.021	0.026	0.021	0.022	0.024	0.019	0.027	0.023	0.024	0.024	0.075
LOI	0.44	0.46	0.42	0.46	0.52	0.52	0.46	0.34	0.46	0.58	0.30
Total	99.76	99.32	99.35	99.30	99.52	98.69	99.52	99.31	99.41	99.62	99.60
fe#	0.904	0.892	0.891	0.898	0.887	0.886	0.871	0.871	0.894	0.885	0.826
ASI	1.026	1.018	1.006	1.013	1.025	1.004	1.000	1.006	1.006	1.035	1.012
Al	0.898	0.884	0.898	0.894	0.880	0.907	0.900	0.894	0.902	0.883	0.846
Li	11.5	17.7	7.98	10.1	13.6	4.22	22.4	22.1	8.02	26.0	36.4
Be	3.04	3.35	3.36	5.57	3.53	2.79	4.28	3.24	3.78	3.35	7.98
Ga*	18	19	19	19	20	19	20	19	19	18	19
Zn*	29	25	24	22	26	35	24	25	46	31	61
Rb	138	132	134	137	155	138	136	130	135	143	164
Sr	57.7	61.3	56.6	54.9	60.1	53.1	56.4	54.9	55.3	52.0	71.8
Y	45.6	45.5	48.3	42.8	125	61.7	43.8	48.9	40.7	88.9	53.4
Zr*	170	183	176	167	176	179	178	183	174	182	300
Nb	20.8	22.0	20.5	18.3	19.3	19.0	23.2	21.3	17.3	21.5	25.6
Cs	1.13	1.38	1.02	1.26	1.46	1.44	1.51	1.54	1.27	1.46	2.26
Ba	647	712	648	640	710	693	700	624	651	694	902
La	73.9	74.2	70.4	66.7	285	87.7	71.7	71.8	73.9	215	74.5
Ce	148	150	144	112	423	172	117	148	145	251	154
Pr	13.3	13.5	13.0	12.4	45.5	16.3	13.2	13.4	13.5	34.0	14.4
Nd	43.1	44.6	42.1	40.3	146	54.2	43.6	43.8	44.1	109	49.2
Sm	7.68	8.18	7.55	7.37	25.8	10.2	8.04	7.97	7.83	19.1	9.32
Eu	0.62	0.71	0.62	0.66	1.61	0.81	0.72	0.64	0.67	1.58	0.95
Gd	7.01	7.47	6.97	6.78	21.9	9.58	7.42	7.23	6.75	15.3	8.26
Tb	1.16	1.21	1.17	1.11	3.26	1.59	1.18	1.21	1.07	2.25	1.34
Dy	7.00	7.07	7.13	6.66	18.4	9.57	6.94	7.29	6.24	12.5	7.93
Ho	1.49	1.48	1.56	1.43	3.65	2.05	1.45	1.55	1.32	2.46	1.68
Er	4.44	4.22	4.60	4.09	9.92	5.83	4.21	4.51	3.77	6.86	4.91
Tm	0.66	0.61	0.67	0.61	1.38	0.86	0.63	0.68	0.55	0.98	0.75
Yb	4.48	4.13	4.52	4.07	8.88	5.55	4.25	4.57	3.66	6.49	5.20
Lu	0.65	0.59	0.66	0.59	1.21	0.78	0.62	0.67	0.53	0.91	0.74
Hf	5.72	5.84	5.47	6.53	6.39	5.85	7.42	6.87	5.80	6.67	8.25
Pb	30.8	24.1	27.2	23.5	25.9	36.4	23.5	26.0	40.8	27.6	37.6
Th	24.5	24.4	23.5	23.0	30.5	25.1	28.0	24.1	22.5	25.9	26.6
U	3.94	2.73	2.94	2.56	3.34	2.25	2.78	2.54	3.15	3.91	4.90
Tsat(zr)	797	802	798	794	799	799	798	801	797	804	843
Tsat(ap)	821	832	817	821	824	800	835	823	828	828	897
A	3.2	2.9	2.9	2.7	3.5	2.8	3.1	2.8	2.8	3.3	3.6

The abundances of Co, Cr, Ni and Sc are all below detection limits, with the exceptions of samples MR-49 and MR-50 with 29.5 and 14.3 ppm of Cr, respectively.

Figure 12: Discriminating chemical diagrams for representative samples, highlighting the main compositional contrasts among the aluminous and peralkaline granites from the Quiriri and Papanduva Plutons, respectively. Available data for other occurrences from the province (Gualda and Vlach 2007a, 2007b, and references therein) are showing in filled and dashed fields for comparisons. **(a)** Alumina Saturation Index [ASI = $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$ mol] vs. Agpaitic Index [AI = $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$ mol]. **(b)** 10^4 Ga/Al (Whalen et al. 1987) vs. AI; labels indicates the I-, S-, M- and A-type granite fields. **(c)** AI vs. fe# number [= $\text{FeO}^{\text{T}}/(\text{FeO}^{\text{T}} + \text{MgO})$, wt.%]. **(d)** AI vs. $\text{Fe}_2\text{O}_3^{\text{T}}/\text{Al}_2\text{O}_3$ molecular ratios. Note the positive linear correlations among ASI, Ga/Al and $\text{Fe}_2\text{O}_3^{\text{T}}/\text{Al}_2\text{O}_3$ with AI. Symbols as in Fig. 5. Comments in the text.

Typical chondritic-normalized trace-element patterns are displayed in Fig. 13. Compared with the Quiriri peraluminous Q1 main granites, which present relatively monotonous patterns, the Papanduva peralkaline granites are relatively enriched in the alkaline metals, Zn, Ga, Th, Nb, Zr, Hf, Y, M-HREE, and depleted in the alkaline-earth metals, P and Ti. The relative enrichment in HFSEs of the peralkaline granites is significant, with Zr, Nb, Y, REE^{T} abundances up to 2430, 88, 320 and 996 ppm, respectively. Among the Quiriri samples, the felsic enclave hosted by the main granite, with lower fe#, as well as the granite porphyries, with higher fe#, tends to present also greater incompatible element abundances. The correlations between selected trace elements contents with

the Agpaitic Index are detailed in Fig. 14. This plot reinforces the above findings and, importantly, depicts the wide variation range and the well-marked positive correlation of most of the LIL and HFS elements with AI as registered in the chemical signature of the peralkaline granites.

Figure 13: Chondrite-normalized multi-element diagram showing relative enrichment and depletion patterns for selected samples from the Quiriri and Papanduva plutons, Morro Redondo Complex. Normalizing factors after Thompson (1982), except Li, Zn and Ga, after McDonough and Sun (1995). Symbols as in Fig. 5. Comments in the text.

Total REE+Y contents vary between ca. 250 and 1150 ppm in the analysed samples and are between ca. 1 and 3 orders of magnitude higher than chondritic values (Fig. 15). The patterns of the main Quiriri granites show a higher fractionation of the LREE over HREE as well as within the LREE and the HREE ranges than the peralkaline Papanduva granites with La_N/Yb_N , La_N/Nd_N and Dy_N/Lu_N ratios between 10-22 and 3-16, 3.1-3.8 and 1.7-3.5 and 1.1-1.5 and 0.7-1.9, respectively. Eu negative anomalies are typical for all samples and well greater in the peralkaline as compared with the peraluminous samples, with Eu/Eu^* [$Eu^* = (Sm_N * Gd_N)^{0.5}$] between 0.11 - 0.15 and 0.21 - 0.28, respectively.

Figure 14: Variation diagrams showing the behavior of selected LIL (a) and HFS (b) elements vs. AI for samples from the Quiriri and Papanduva Plutons, Morro Redondo Complex. Comments in the text.

On the whole, the geochemical signatures of the samples from the Quiriri Pluton are very akin with other peraluminous rocks from the aluminous association in the Graciosa Province (e.g. Gualda and Vlach 2007a, Vlach and Gualda 2007, cf. Fig. 12); however, with the exception of the felsic enclave, rocks with $\text{SiO}_2 < 74.4$ wt. % are lacking in this pluton (cf. Table II). The peralkaline alkali-feldspar

granites from the Papanduva Pluton, on the other hand, include the most evolved peralkaline rocks that constitute the alkaline association in the province.

Figure 15: REE patterns for selected samples from the Quiriri and Papanduva Plutons, Morro Redondo Complex. Normalizing factors after Boynton (1984). Symbols as in Fig. 5. See the text.

8. RADIOGENIC HEAT PRODUCTION

Radiogenic heat is generated by the decay of radioactive isotopes ^{40}K , ^{232}Th , ^{235}U and ^{238}U and is directly related to the chemical and thermal evolution of the crust (e.g., Jaupart and Mareschal 1999, 2010, Bea 2012). Heat energy enhances hydrothermal circulation and high heat production (HHP) granites are often associated with ore deposits and geothermal anomalies. Representative heat productions per unit volume (A) due to the Morro Redondo intrusive rocks are presented in Table II.

Heat productions vary from 1.6 to 5.7 μWm^{-3} with a mean about 3.3 μWm^{-3} (Fig. 16). The peralkaline granites from the Papanduva Pluton show both minimum and maximum values, and a greater mean (3.6 μWm^{-3}), when compared to syenogranites from the Quiriri Pluton, with a narrow variation range (2.6 - 3.5 μWm^{-3}) and a mean about 3.0 μWm^{-3} . The felsic microgranular enclave hosted by the main Quiriri granite gives 3.6 μWm^{-3} . These rates are well higher than the typical values for upper and middle crusts (ca. 1.7 and 1.0 μWm^{-3}), the medium values founded in common

granites and rhyolites (ca. $2.5 \mu\text{Wm}^{-3}$, cf. Rybach 1988, Haenel et al. 1988, Kemp and Hawkesworth 2003), as well as those observed for other occurrences in the province (our unpublished data). The highest A computed values for Papanduva cataclastic and protomylonitic peralkaline facies (4.2 - $5.7 \mu\text{Wm}^{-3}$, mean about $4.7 \mu\text{Wm}^{-3}$) approach those most typical for HHP granites elsewhere.

Figure 16: Histogram showing typical values for the radiogenic heat production (A) for selected samples from the Quiriri and Papanduva plutons, Morro Redondo Complex. Comments in the text.

9. CRYSTALLIZATION CONDITIONS

The quantification of the intensive parameters related to the emplacement and crystallization of magmas that formed the granitic and related rocks from the Graciosa Province is not an easy task, due to the lack of appropriate mineral assemblages and/or the intense late- to post-magmatic transformations (e.g. Vlach and Gualda 2007, Anderson et al. 2008). Any case, a qualitative assessment may be drawn, as detailed in the following.

9.1. LITHOSTATIC PRESSURE AND TEMPERATURES

Gualda and Vlach (2007a) emphasize that geological and petrographic evidences indicate that the emplacement of plutons from the Graciosa province are incompatible with confining pressures higher than ca. 2 kbar, an observation which is also in accordance to available gravimetric data (Hallinan et al. 1993). The scenario is not different in the Morro Redondo Complex

case, were the association of coeval plutonic and volcanic rocks, the presence of vugs, miarolitic cavities, volcanic xenoliths, as well as of granophyric intergrowths, in the granites point to crystallization in shallow crustal levels. Our Ab-Or-Qz normative data also supports this inference (Fig. 11).

The assemblage biotite + hornblende + titanite + Fe-Ti oxides (+ quartz + alkali feldspar + plagioclase) in samples from the Quiriri Pluton allows the application of the Al-in-hornblende geobarometer of Anderson and Smith (1995), as calibrated with the plagioclase-hornblende thermometry of Holland and Blundy (1994). Our results are between 0.6 and 1.2 kbar with a mean value of 0.8 (± 0.2) kbar (Fig. 17a), which seems to be reasonable, in agreement with estimated confining pressures for other shallow alkaline massifs and complexes worldwide (e.g. Larsen and Sørensen 1987, Potter et al. 2004, Mann et al. 2006). However, this value may be underestimated, given that plagioclase compositions are relatively sodic (An_{8-27}) and so the expected Al^{IV} contents in hornblende will be lower than those observed in calibrated experiments (Anderson and Smith 1995).

Zircon and apatite saturation temperatures were estimated for Quiriri samples following Watson and Harrison (1983, see also Hanchar and Watson 2003 and Miller et al. 2003) and Harrison and Watson 1984 (see also Pichavant et al. 1992). Results are presented in Table II. All samples are within the calibrated range specified by Miller et al. (2003), with a M factor [$= (Na+K+2Ca)/(Al \cdot Si)$, in cations] between 1.36 and 1.46. The evaluated temperatures vary from 794 to 860 °C, with a mean of 807 °C (Fig. 17b). Most samples gave temperatures close to 800 °C, a value significantly lower than temperature estimates obtained for similar plutons from the Graciosa Province (Gualda and Vlach 2007a) and A-type granites worldwide (e.g. Poitrasson et al. 1995, King et al. 1997, King et al. 2001), in the range 850 - 900 °C. Apatite saturation temperatures are always higher (800 - 897 °C), with a mean of 834 °C. The felsic enclave has zircon and apatite saturation temperatures of 847 and 897 °C, respectively (Fig. 17b).

Plagioclase-hornblende equilibrium temperatures were computed according to Holland and Blundy (1994), based on the reaction edenite + albite $\leftrightarrow$ richterite + anorthite (see Anderson 1996). The obtained values vary within 629 - 655 °C, with a mean about 643 (± 4) °C (Fig. 17a). These are

also qualitative estimates due to the high $fe\#$ values of Ca-amphiboles. Any case, they partially overlap the temperatures derived from the plagioclase - alkali feldspar solvus (500 - 650 °C, Fig. 9) and are consistent with the expected close-to-solidus temperatures in such granitic systems.

In the peralkaline rocks like those from the Papanduva Pluton, any estimate of zircon or apatite saturation temperatures may result in meaningless values (e.g. Watson 1979, Keppler 1993, Miller et al. 2003). Although some authors argue that the crystallization of mineral phases as Na-amphiboles and pyroxenes may allow magmas to turn saturated in Zr (cf. Watson 1979, Hanchar and Watson 2003) and others had considered the calculated zircon saturation temperatures reasonable (e.g. Shellnutt and Iizuka 2011), in these systems, even if zircon is a crystallizing phase and the M parameter is within the calibration range of Watson and Harrison (1983), Zr does not necessarily behave as an essential structural trace element, as it may be incorporated also in other essential or accessory minerals in significant amounts. Also, the positive correlation between Al and Zr contents in our samples indicates that Zr solubility had increased with peralkalinity. For instance, in the zircon-bearing samples from the massive and microgranitic facies, the zircon saturation temperatures are between 880 and 970 °C, with a mean about 930 °C (Fig. 17b). Although these values are not out of the expected range for some “dry” A-type granites (e.g. Clemens et al 1986, White et al 2005), they appear to be in disagreement with several evidences from peralkaline volcanic systems worldwide (cf. Macdonald 2012 and references therein).

Qualitative estimates of the solidus temperature for the Papanduva Pluton can be obtained from the mineral assemblage. Because of the presence of Fe-richterite and arfvedsonite, as well as aenigmatite as an important magmatic accessory phase, maximum solidus temperatures are suggested to fall in the interval between 700 - 750 °C (e.g. Ernst 1968, Thompson and Chisholm 1969, Scaillet and MacDonald 2001), in agreement with alkali feldspar solvus estimates, between 650 - 750 °C (Vilalva 2007).

Figure 17: Thermobarometric estimates for the Morro Redondo Complex. **(a)** Plagioclase-hornblende thermometry estimates (T °C) of Holland and Blundy (1994) vs. Al-in-hornblende barometric estimates (P kbar) of Anderson and Smith (1995) for the Quiriri Pluton. Uncertainty lines in T and P in each estimative represents 1σ precision error. **(b)** Zirconium-Saturation Thermometry estimates (T_{Zr} °C) of Watson and Harrison (1983) vs. Apatite Saturation Thermometry estimates (T_{ap} °C) of Harrison and Watson (1984) for the Papanduva and Quiriri Plutons.

9.2. REDOX CONDITIONS

The mineral assemblages and mafic silicate compositions observed in the granites from the Quiriri Pluton point to relatively oxidizing crystallization conditions. The paragenesis biotite $\pm$ Ca-amphibole + quartz + titanite + magnetite $\pm$ ilmenite indicates f_{O_2} conditions close or higher than the TMQAI [titanite – magnetite – quartz – amphibole (Fe-tremolite) – ilmenite] buffer (Noyes et al. 1983, Wones 1989), for which precise thermodynamic parameters were not well established yet. The $fe\#$ number [$= Fe^T / (Fe^T + Mg)$, cations] of biotite and amphiboles leads to a similar conclusion. The equilibrium:

where a stands for the activity of the indicated component in the main mineral solid solutions, was studied and calibrated by Wones (1981). It indicates that for a given f_{H_2O} , the higher the oxidation state, the lower the expected annite content within biotite, as the equilibrium will shift to

the high. Similar reasoning may be applied to the $fe\#$ values observed in Ca-amphiboles (e.g. Anderson and Smith 1995). Using this equilibrium and a large data set including independent f_{O_2} determinations and $fe\#$ numbers in biotite from magnetite-bearing Mesoproterozoic granites from Laurentia (USA), Anderson et al. (2008) estimated Δ_{QFM} values as a function of the biotite $fe\#$ number. Our compositions, mostly with $0.6 \leq fe\# \leq 0.7$, give $\Delta_{QFM} \approx +1$, a value one or two units lower than the estimates based on the TMQAI equilibrium (Vlach and Gualda 2007). The $fe\#$ numbers measured in Ca-amphibole, down to 0.4, point also to relatively high oxidizing conditions (Anderson and Smith 1995).

The stability of Na-Ca and Na-amphiboles in the peralkaline granites from the Papanduva Pluton suggest relatively reduced crystallization conditions, between the MW (Magnetite - Wüstite) and QFM (Quartz - Fayalite - Magnetite) buffers (Ernst 1968, Stolz 1986, Marks et al. 2003, Pe-Piper 2007). Such conditions turn progressively more oxidizing as crystallization proceeds and the occurrence of aenigmatite in an antipathetic relation with Fe-Ti oxides, a typical feature of several samples from the Papanduva Pluton, suggests crystallization inside the “no-oxide field”, an area in the T- f_{O_2} space where aenigmatite, aegirine and quartz coexist in the absence of Fe-Ti oxides, that is located above the QFM buffer in super-saturated rocks (Nicholls and Carmichael (1969, see also Vilalva 2007). Moreover, the relative stability of Na-amphiboles and aegirine depends on f_{O_2} , f_{H_2O} , and the availability of Na meta- and di-silicates hypothetical molecules in the melt, as described by the equilibrium:

and a similar one relating aegirine to arfvedsonite (Bailey 1969, see also Deer et al. 1978). This reaction show that in aenigmatite-absent rocks, the late- to post-magmatic crystallization of aegirine, as isolated crystals or mantles over amphiboles, is favored in more oxidizing environments, limited by QFM and HM buffers (Bailey 1969).

10. SUMMARY AND FINAL REMARKS

The Morro Redondo Complex, one of the largest complexes in the Graciosa Province, is composed of high-SiO₂ rocks from the alkaline and aluminous associations of A-type granites that had formed two contrasting plutons denominated Papanduva and Quiriri, as well as coeval acid and basic to intermediate volcanic rocks. Scarce field evidence suggest that granites emplaced somewhat after the volcanic rocks and that at least some peralkaline rocks were emplaced after the main aluminous ones.

The Papanduva Pluton is made of *hypersolvus* aegirine ± arfvedsonite - alkali feldspar granites with a variety of structural, textural and mineralogical properties, including massif, cataclastic and protomylonitic petrographic facies, presenting low magnetic susceptibilities, formed in relatively reduced environments. They are among the most evolved peralkaline rocks known all over the Graciosa Province, with Agpaitic Indexes up to ca. 1.3, the highest Na and Fe³⁺ contents in Na-amphiboles and clinopyroxenes and the highest LILE and HFSE abundances, which correlates positively with the peralkalinity grade, as measured by the Agpaitic Index. Such particular geochemical signature leads to the development of rare “agpaitic” nature of its more evolved facies, as evidenced by the Ti-, Zr- and REE-rich unusual accessory mineralogy, which had crystallized during late- to post-magmatic crystallization stages. In fact, textural relationship between mafic and felsic minerals indicate that these rocks followed an agpaitic crystallization sequence (e.g. Sørensen 1997, Andersen et al. 2010), in which the main and accessory mafic phases appear after quartz and alkali feldspar. It is worth to note that several among these minerals (e.g. aenigmatite, neptunite, narsarsukite, Na-K zirconosilicates, nacareniobsite, turkestanite, as well as some still unidentified phases, cf. Vilalva and Vlach 2010, Vlach and Vilalva 2007, Vilalva and Vlach 2006) were described for the first time in peralkaline granites from Brazil. Such mineralogy and texture, as well as the geochemical data, indicates that the more evolved the liquids, the more higher the Agpaitic Index, as well as the Na₂O, Fe₂O₃^T, LILE and HFSE abundances.

The Quiriri Pluton is the largest in extent and comprises mainly *subsolvus* biotite ± hornblende sienogranites slightly peraluminous (1.05 < ASI < 1.20) granites as well as granite porphyries with higher magnetic susceptibilities, formed under relatively oxidizing conditions. As for

most of the rocks in the aluminous association in the province (Gualda and Vlach 2007a, Vlach and Gualda 2007), the granites have homogeneous compositions, with relatively lower $fe\#$ numbers and $Fe_2O_3^T/Al_2O_3$ molecular ratios and higher Ca and alkaline earth metals, and are characterized by relatively Ca- and Al-rich mafic mineral paragenesis, given by annitic biotite $\pm$ hornblende + titanite $\pm$ allanite + magnetite + ilmenite + fluorite (+ apatite + zircon). As a consequence, biotite and hornblende from these rocks show little chemical variations, as compared with the amphiboles and clinopyroxenes from the peralkaline rocks. A remarkable feature of many samples from the Quiriri Pluton is the hydrothermal alteration which may be locally pervasive and in which some sulfides are seen.

Both plutons are characterized by relatively high heat productions. The higher mean as well as punctual values (up to $5.7 \mu W m^{-3}$) are identified in peralkaline, protomylonitic, granite types and approach values found in typical HHP granites worldwide. Such characteristics reflect the geochemical signatures of the studied granites and are features mostly attributed to inheritance from their source rocks, later enhanced by magmatic fractionation processes.

Geological and petrographic evidences indicate that both plutons were emplaced at shallow crustal levels. Semi-quantitative pressure estimates for the hornblende-bearing samples from Quiriri, are about 1.0 kbar. Estimated close-to-liquidus temperatures for the Quiriri main granites gave about 800 and 850 °C, while the felsic monzogranitic enclave gave ca. 850 and 900 °C, the higher values found through apatite saturation estimates. The presence of ubiquitous apatite inclusions in zircon (Vilalva et al. unpublished data) suggest that apatite may be a liquidus phase, while zircon was coeval or somewhat late. On the whole, these zircon saturation temperatures are somewhat lower than those observed in similar granites from the Serra da Graciosa region (Gualda and Vlach, 2007a). Considering close-to-solidus temperature estimates in the main granites ca. 650 °C, the melts crystallization range was about 200-250 °C. Given the peralkaline nature of the Papanduva melts, it is difficult to attribute confidence to zircon saturation temperature estimates (up to 970 °C). Based on some data from alkaline rhyolite occurrences and laboratory experiments

(Macdonald 2012, Scaillet and Macdonald 2001), we suggest a crystallization interval between ca. 800 and 600°C for the peralkaline melts.

Ti-in-quartz temperatures (Wark and Watson 2006) in representative samples gave mean values about 740 and 830 (± 20) °C for the main granites and the felsic enclave from the Quiriri Pluton and 715 (± 20) °C for peralkaline samples from the Papanduva Pluton (our unpublished data). With the exception of the felsic monzogranitic enclave, such temperatures appear to be somewhat underestimated when compared with the saturation temperature estimates for the aluminous granites, as in fact, quartz was expected to be a relatively early crystallization phase considering the involved textures, rock compositions and emplacement pressures.

The peralkaline melts crystallized arguably under fO_2 conditions close or slightly below the QFM buffer, some of them within the “no-oxide” field of Nicholls and Carmichael (1969). Amphibole and clinopyroxene compositional variations, as well the development of aegirine mantles over amphibole, indicate that the crystallization had followed an oxidizing path, ending close to the HM buffer in the post-magmatic stage, a common feature of most peralkaline occurrences in the Graciosa Province (e.g. Vlach and Gualda 2007). Melts that formed the Quiriri granites crystallized, by its turn, in higher oxidizing conditions ($\Delta_{QFM} \geq 1$), close to the TMQAI buffer (Noyes et al. 1983, Wones, 1989). Their evolution also followed an oxidation path.

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RESUMO

O Complexo Morro Redondo é uma das ocorrências mais importantes da Província Graciosa de tipo-A, S do Brasil. O complexo é formado por dois plutons distintos, denominados Papanduva e Quiriri e rochas vulcânicas bimodais contemporâneas. O Plúton Papanduva inclui álcali-feldspato granites peralcalinos massivos e deformados, com anfibólios de Na-Ca e clinopiroxênios de Na. Os tipos deformados são as rochas peralcalinas mais evoluídas na província and contêm minerais “agpaíticos” raros, alguns descritos pela primeira vez em granitos do Brasil. O Plúton Quiriri, maior, é constituído por biotita sieno- e monzogranitos levemente peraluminosos, maciços, com raro anfibólio de Ca. As composições da biotita do Quiriri são relativamente homogêneas, enquanto os anfibólios e piroxênios do Papanduva mostram caminhos evolutivos com aumento em Na e Fe^{3+} . Os granitos Morro Redondo são ferroanos, com teores elevados em SiO_2 , álcalis e HFSE. Nos tipos peralcalinos, com os maiores valores $\text{Fe}^\#$, os conteúdos de LILE e HFSE aumentam com o Índice Agpaítico e os mais evoluídos são granitos HHP, com produção de calor radiogênico de até $5.7 \mu\text{Wm}^{-3}$. Estimativas geotermobarométricas indicam colocação magmática sob baixas P (≈ 1 kbar) , em temperaturas de até $850 - 800^\circ\text{C}$, em condições relativamente reduzidas (QFM) e oxidantes ($+1 < \Delta_{\text{QFM}} < +3$) para os Plútons Papanduva e Quiriri, respectivamente. Em ambos os casos, os magmas evoluíram para condições mais oxidantes conforme sua cristalização progrediu.

PALAVRAS-CHAVE: Petrografia, Mineralogia, Geoquímica, Granitos de tipo-A, Morro Redondo Complex, Província Graciosa.

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ANEXO:

B

IN-SITU U-Pb DATING AND TRACE ELEMENT COMPOSITIONS OF ZIRCON FROM THE GRACIOSA A-TYPE PROVINCE, SOUTH BRAZIL: INSIGHTS FOR THE TIMING OF EXTENSIONAL MAGMATISM AT END OF THE BRASILIANO-PAN-AFRICAN OROGENY

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ABSTRACT

Combined in-situ trace element compositions and U-Pb dates were obtained by LA-ICP-MS for zircons from a suite of granitic and syenitic plutons exhibiting peralkaline and metaluminous to slightly peraluminous affinity, and from a peralkaline rhyolite all within the Graciosa A-type Province, southern Brazil. The results indicate emplacement ages of 582 ± 5 Ma and 567 ± 7 Ma for the peralkaline granites of Papanduva and Mandira Plutons, respectively; zircons contain high contents of LREE, Hf, as well as U and Pb. Zircons from the rhyolite are characterized by low LREE and high Hf, Th, U and Pb abundances and yield an age of 585 ± 5 Ma. The ages for the emplacement of the metaluminous syenites of the Corupá Pluton range between $580 (\pm 6)$ and $586 (\pm 7)$ Ma. For the metaluminous to slightly peraluminous granites, emplacement ages vary between $584 (\pm 6)$ and $586 (\pm 6)$ Ma for the Quriri and Guaraú Plutons, with a slightly older age of 593 ± 9 Ma for the Alto Turvo Pluton. Zircons record higher HREE and Th abundances in the syenites, whereas in the aluminous granites they are REE-poor and Hf-rich. Overall, the geochronological data suggest that the emplacement of the peralkaline granites and metaluminous syenites of alkaline affinity occurred shortly after that of the metaluminous to slightly peraluminous granites. Moreover, a younger age population at ca. 562 – 567 Ma is discernable for most of the samples of peralkaline and aluminous granites and for the metaluminous syenites. Textural and chemical evidences for zircons within the peralkaline granites suggest that these younger ages relate to a late-stage, post-magmatic/hydrothermal alteration event. In contrast, the younger-aged zircons within the syenites

and aluminous granites may represent final crystallization ages, and therefore suggests a protracted magmatic history of up to 10 Ma, rather than a single or very short-lived magmatic event giving rise to these intrusive rocks.

Key-words: A-type magmatism, post-collisional, U-Pb LA-ICP-MS, Graciosa Province, Brasiliano – Pan-African Orogeny, pluton emplacement

1. INTRODUCTION

According to Liégeois (1998), post-collisional geodynamic settings represent a complex period of time that can include many geological events within a continuous or episodic extensional regime where various types of magmatism can occur. There still remains much debate in relation to the exact definition of ‘A-type’ rocks, their sources-areas, evolutionary trends, and various modes of emplacement, this more than 30 years after the pioneering work by Loiselle and Wones (1979). A-type magmatism, besides being typical of anorogenic environments, has been consistently associated with extensional post-collisional settings (see review in Bonin, 2007). In this context, the exact timing of emplacement and crystallization of these anorogenic rocks following a collisional cycle require accurate and precise absolute age determinations in order to formulate tectonic evolutionary models. The geochronological constraints may then identify distinct magmatic events that are typically separated by short time intervals (<5 Myr), which are usually within the range of the analytical uncertainty associated with the in-situ dating method employed here.

The abundance of A-type intrusive bodies within the Graciosa Province, southern Brazil (Gualda and Vlach, 2007a) provides an ideal setting to investigate the evolution, composition and geotectonic significance of A-type granitoids and associated rocks (e.g. Garin et al., 2003; Gualda and Vlach, 2007a, 2007b, 2007c; Vlach and Gualda, 2007; Vilalva and Vlach, 2010, Vlach et al., 2011). The Graciosa province was formed in an extensional, post-collisional regime that followed the amalgamation of the Gondwana supercontinent, at the waning stages of the Brasiliano-Pan-African Orogeny. As discussed by Vlach et al. (2011), the province has been subject of

geochronological studies over the last few decades that yielded a large amount of age data obtained using K-Ar, Rb-Sr and U-Pb (mainly ID-TIMS) dating methods (e.g. Cordani, 1974; Siga Jr. et al., 1997; Cordani et al., 2000; Weber et al., 2001; Passarelli et al., 2004; Basei et al., 2009; Vlach et al., 2011). In most cases, however, the available ages, ranging between 620 and 570 Ma, are associated with large uncertainties, in part associated to the complex zircon evolutionary history due to the presence of inherited components and late- to post-magmatic effects, mainly in the more differentiated granitic and syenitic rocks. The older ages, in fact, overlap most of the ages of syn-to-late-collisional high-K calc-alkaline batholiths that crop out in the same region (e.g. Harara, unpublished data; Vlach et al., 2011). Trying to solve such a problem, Vlach et al. (2011) conducted ID-TIMS dating in contemporaneous dioritic rocks. The authors successfully obtained much more precise ages at 580 ± 2 and 583 ± 2 Ma.

Combined in-situ U-Pb age determinations and trace element analyses using laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful technique since it determines the abundances of important trace elements within zircon, such as U, Th, Pb, Hf and rare-earth elements (REEs), in the same spot where the age determination was achieved. This integrated approach can surely solve many of the problems pointed out above, as preliminary shown by zircon LA-ICP-MS dating by Braun et al. (2010), leading the authors to recognize three different concordant age populations corresponding to components of inheritance, magmatism and hydrothermal alteration. Subsequent employment of this combined method was also conducted by Koch et al. (2011) and Vlach et al. (2012).

Hence, this study presents the results from a combined investigation involving in-situ LA-ICP-MS U-Pb dating and trace element composition of zircon from various A-type granitic and syenitic plutons, as well as a contemporaneous rhyolite from the Graciosa Province. This novel data provide new insights into the emplacement, evolution and final crystallization of the magmas giving rise to the Graciosa province, the late-stage to post-magmatic events, and the relationship with the geodynamic settings at the end of the Brasiliano – Pan-African Orogenic Cycle in the southern Brazil.

2. GEOLOGICAL BACKGROUND

The Graciosa Province is recognized for its typical A-type post-collisional magmatism formed during an extensional period after the consolidation of crustal blocks (Fig. 1); this occurred during the terminal phase of the Brasiliano – Pan-African Orogeny that resulted in the formation of the Gondwana supercontinent (Gualda and Vlach, 2007a). The province is made of several A-type granitic and syenitic plutons showing roughly circular to irregular outlines, as well as associated basic, intermediate and acid volcanics, gabbroic, dioritic and hybrid rocks (Fig. 1). The plutons are believed to have been emplaced at shallow crustal levels along a broad NE-SW-trending arc parallel to the present-day coast line, and intrude Archean rocks of the Luis Alves Microplate and Paleo- to Neoproterozoic rocks of the Curitiba Microplate and Paranaguá Terrain (e.g. Siga Jr. et al., 1993; Basei et al., 2009).

The plutons are grouped into two distinct primary petrographic associations, either alkaline or aluminous affinities, which resemble other A-type provinces world-wide (e.g. Lameyre and Bowden, 1982; Pitcher, 1993; King et al., 1997). The alkaline association is composed of metaluminous alkali-feldspar syenites to peralkaline hypersolvus granites formed under relatively reducing conditions, close to the Quartz-Fayalite-Magnetite (QFM) buffer (Gualda and Vlach, 2007a, Vilalva, 2007; Vlach et al., 2011). The more evolved varieties of peralkaline granites show a distinct “agpaitic” character (e.g. Vilalva and Vlach, 2006; 2010). In contrast, the aluminous association comprises metaluminous to moderately peraluminous subsolvus syeno- and monzogranites formed under more oxidizing conditions. Rapakivi textures appear in several plutons belonging to this group.

Figure 1: Simplified geologic map of Southern Brazil, between the states of São Paulo and Santa Catarina, showing the distribution of the plutons that form the A-type Graciosa Province. Main tectonic domains are: A – Apiaí (Paleo- to Mesoproterozoic); B – Curitiba (Paleo- to Neoproterozoic); C – Luiz Alves (Archean to Paleoproterozoic) and D – Paranaguá (Neoproterozoic). Main transcurrent shear zones are: LCSZ – Lancinha-Cubatão; MPSZ – Mandirituba-Piraquara; RPSRSZ – Rio Palmital-Serrinha and PTSZ – Tijucas. I: Neoproterozoic volcano-sedimentary basins; II: A-type granites and syenites of the Graciosa Province (1- Serra do Paratiú, 2- Guaraú, 3- Mandira, 4- Ilha do Cardoso, 5- Alto Turvo. Serra da Graciosa region: 6- Capivari, 7- Órgãos, 8- Farinha Seca, 9- Anhangava and 10- Marumbi. 11- Serra da Igreja, 12- Morro Redondo Complex, 13- Palermo, 14- Agudos do Sul, 15- Rio Negro, 16- Dona Francisca, 17- Piraí, 18- Serra Alta and 13- Corupá); III: Granitic stocks with A-type affinity of the Apiaí Domain; IV: Piên Mandirituba calc-alkaline Batholith; V: Paranaguá Batholith; VI: Três Córregos Batholith and associated granitic stocks. Adapted and modified from Harara (unpublished), Prazeres Filho et al. (2003), Heilbron et al. (2004), Gualda and Vlach (2007a) and Vlach et al. (2011). Studied samples are represented by white stars.

Small intrusive bodies and dykes of gabbro, diorite and hybrid rocks are found intruding the granitic and syenitic rocks (Gualda and Vlach, 2007a). Contrarily, a bimodal volcanic sequence

including basalts, andesi-basalts and rhyolites is spatially and temporally associated with the intrusive rocks in some plutons (Góis and Machado, 1992), and also in contemporaneous volcano-sedimentary basins, such as the Campo Alegre and Guaratubinha basins (Citroni et al., 2001; Basei et al., 2009; Almeida et al., 2010).

3. SAMPLE CHARACTERIZATION

A total of ten samples consisting of granite and syenite from both alkaline and aluminous associations, as well as one sample of an associated and contemporaneous rhyolite were selected for this study. Representative samples of the alkaline association are from the Papanduva (Morro Redondo Complex), Mandira and Corupá Plutons, while samples of the aluminous association were retrieved from the Quiriri (Morro Redondo Complex), Guaraú and Alto Turvo Plutons (Fig. 1).

3.1. ALKALINE ASSOCIATION

Samples from the Papanduva Pluton, which belongs to the Morro Redondo Complex (sample MR-39) and occurs within the southern area of the Graciosa Province, and from the Mandira Pluton (sample MAN-13A) located in the northern region of the province (Fig. 1), are both classified as hypersolvus alkali-feldspar granites. These samples are peralkaline in composition with $0.73 < A/NK [Al_2O_3/(CaO+Na_2O+K_2O)mol.] < 0.97$ and $0.76 < A/NK [Al_2O_3/(Na_2O+K_2O)mol.] < 0.98$. They are both massive, holo- to leucocratic rocks (color index – $M' < 5$) light-gray in color, and exhibit fine- to medium-grained hypidiomorphic textures. The main mafic minerals are interstitial sodic amphiboles (arfvedsonite and riebeckite) in the Papanduva and Mandira Plutons and clinopyroxene (aegirine) only in the Papanduva Pluton. Accessory minerals include a variety of rare “agpaitic”, HFSE-rich phases, mainly in the Papanduva Pluton, include astrophyllite and aenigmatite, as well as zircon and chevkinite. Rounded milli- to centimetric mafic enclaves are rare in the Papanduva Pluton.

In the southernmost part of the province, three samples (CO-32C, CO-32D and CO-38) were selected from the Corupá Pluton (Fig. 1) and these represent different varieties of syenite. The samples are massive alkali-feldspar syenites of metaluminous to slightly peralkaline character ($0.61 < A/CNK < 0.88$; $1.02 < A/NK < 1.13$), with medium- to coarse-grained hypidiomorphic textures. In general, these samples are pink-colored, alkali-feldspar syenites with hedenbergite to aegirine-augite and calcic to sodic-calcic amphiboles, which are the most common type within the pluton (e.g., sample CO-38). Sample CO-32C represents an oversaturated ($SiO_2 = 61.9$ wt.%), green-colored, leucocratic ($5 < M' < 15$) rock with hedenbergite, sodic to sodic-calcic amphiboles and fayalite; whereas sample CO-32D is a saturated melanocratic ($M' > 50$) melasyenite containing hedenbergite, Fe-hornolite and biotite as the main mafic phases, as well as a significant amount of magnetite. The latter occurs locally as centimetric bands exhibiting cumulate textures and is intercalated with the green syenite (e.g., sample CO-32C). In all cases, in addition to zircon, chevkinite, ilmenite, and apatite are the most common accessory minerals.

The rhyolite sample (MR-254) investigated here is from the Morro Redondo Complex, and consists as part of a contemporaneous bimodal volcanic sequence that crops out mainly close to the NW and central portions of the complex (Fig. 1). The peralkaline rhyolites are interpreted as being petrogenetically related to the granites of the Papanduva Pluton. The rhyolite is a massive, hololeucocratic ($M' = 4$) rock characterized by a porphyritic texture defined by tabular potassic feldspar and globular quartz megacrystals set within a fine-grained, reddish, quartz-feldspatic matrix with sodic and sodic-calcic amphiboles as the main mafic minerals. The rhyolite is also present as irregular, centimetric-sized xenoliths within the Papanduva Pluton.

3.2. ALUMINOUS ASSOCIATION

Three samples (MR-161, MR-186A and MR-201A) from the Quiriri Pluton were taken from the south and central portions of the Morro Redondo Complex. These are all massive, holo- to leucocratic ($4 < M' < 7$), pink-colored, medium-grained biotite syenogranites with hypidiomorphic

textures and slightly peraluminous signature ($1.0 < A/CNK < 1.04$; $1.11 < A/NK < 1.13$). Magnetite, titanite, fluorite, apatite and zircon are common accessory minerals, while chlorite and epidote are important secondary minerals that are replacing biotite in samples MR-161 and MR-201A as result of late-stage hydrothermal alteration. Centimetric, irregular to round-shaped microgranular mafic and felsic (granitic) enclaves are relatively common.

Sample GUA-16 corresponds to the main granite-type from the Guaraú Pluton (Fig. 1): massive, leucocratic ($M' \approx 7$), white to light-pink, fine- to medium-grained biotite alkali-feldspar granite with hypidiomorphic textures and a metaluminous character ($A/CNK \approx 0.98$; $A/NK \approx 1.6$). Magnetite, zircon and some sphalerite and topaz are accessory minerals.

Sample AT-15C from the Alto Turvo Pluton (Fig. 1) corresponds to a massive, leucocratic ($6 < IC < 7$), light-pink, coarse-grained biotite monzogranite showing hipidiomorphic textures and a metaluminous to slightly peraluminous signature ($A/CNK \approx 0.98$; $A/NK \approx 1.2$).

4. ANALYTICAL METHODS

4.1. ZIRCON SELECTION

Fractions of *ca.* 25 – 50 euhedral zircons and crystal fragments were obtained from 3 to 5 Kg for each sample following the procedures described in Vlach et al. (2011). In order to guide the selection of areas for trace element and U-Pb data acquisition, cathodoluminescence (CL) and secondary electron (SE) imaging of the selected crystals were conducted at the Centro de Pesquisas Geocronológicas (CPGeo) of the Instituto de Geociências (IGc), Universidade de São Paulo (USP), Brazil.

4.2. LA-ICP-MS TRACE ELEMENT ANALYSES

In-situ trace element abundances were obtained using a ThermoFinnigan high resolution Element2 ICP-MS instrument coupled to a New Wave Research UP213 laser ablation system located at MITERAC facility, University of Notre Dame (USA), and the Elan 6100DRC ICP-MS instrument coupled to the UP213 laser ablation system at the IGc – USP. A spot size of 30 μm , with a repetition rate of 4 Hz and power output of 70%, corresponding to an energy density of ca. 10 J/cm^2 were used for both instruments. Trace element analyses were conducted, when possible, in the same spots where U-Pb age determinations were determined. Total acquisition time was 120 seconds, which was equally divided between acquisition of background and laser ablation ion signal measurements. The NIST SRM 612 glass was used as the external calibration standard, and an average SiO_2 abundance of 31.6 wt.%, based on electron microprobe (EPMA) analyses of zircons from the Graciosa Province (S.R.F. Vlach, unpublished data), was chosen as the internal standard. Data reduction and calculation of elemental abundances were achieved using the *Glitter* software (Van Achterbergh et al., 2001). Details of the analytical protocol employed at MITERAC is described in Simonetti and Neal (2010, supplementary materials and references therein).

4.3. LA-ICP-MS U-Pb DATING

In-situ U-Pb age determinations were conducted at MITERAC using the identical instrumentation cited above. Laser ablation analyses were conducted using a spot size of 30 μm , with a laser repetition rate of 4 Hz and a laser output of 55%, corresponding to an energy density of ca. 4-5 J/cm^2 . Individual measurements were completed after 75 seconds, which consisted of the first 30 seconds for measurement of the background, followed by 30 seconds of laser ablation data acquisition, and followed by 15 seconds of washout time. Correction for laser induced elemental fractionation (LIEF) was achieved by repeated analysis of the international zircon standard BR266 (Stern and Amelin, 2003) subsequent every 15 unknown measurements using a ‘standard-sample’ bracketing technique. Isoplot (versions 4.0 and 3.7; Ludwig, 2003) was used for data reduction and

plotting of radiogenic-isotope data. A detailed description of the in-situ U-Pb dating technique and the employed analytical protocols can be found in Simonetti and Neal (2010).

5. ZIRCON CRYSTAL MORPHOLOGY AND TRACE ELEMENT COMPOSITIONS

Selected zircon crystals representative of the analyzed samples are shown in Figs. 2 and 3, while representative trace element compositions of zircons are listed in Table 1. The entire data set is available as supplementary material. The main textural and chemical characteristics are discussed below.

5.1. ALKALINE ASSOCIATION

5.1.1. Granites

Textures

Zircon in peralkaline granites from Papanduva (sample MR-39) and Mandira Plutons (sample MAN-13A) occurs as subhedral to euhedral, medium-to-large grains (100 – 300 μm diameter) with well-developed {100}-prism and {101}-pyramid surfaces, typical of zircons from alkaline series granites (Pupin, 1980). Cathodoluminescence (CL) imaging reveals well-marked zoning, mainly in the outer portions of the grains, and internal evidences for subsolidus alteration, such as dissolution, embayment and recrystallization. Most of the grains consist of euhedral cores with variable CL intensities, including weak-to-moderate and high CL contrasts. Inherited cores with very weak CL are less common (Figs. 2a, b).

Figure 2: Cathodoluminescence (CL) images of zircons from various A-type granitic and syenitic plutons and associated rhyolite of the alkaline association of the Graciosa Province. In-situ U-Pb analyses are identified by circles with correspondent absolute $^{206}\text{U}/^{238}\text{Pb}$ age (2σ error). Scale bar = 200 μm .

Figure 3: Cathodoluminescence (CL) images of zircons from various A-type granitic plutons of the aluminous association of the Graciosa Province. In-situ U-Pb analyses are identified by circles with correspondent absolute $^{206}\text{U}/^{238}\text{Pb}$ age (2σ error), except for the inherited core presented in (e), where the value (*) represents the absolute $^{207}\text{Pb}/^{206}\text{Pb}$ age (2σ error). Scale bar = 200 μm .

The cores exhibit cracking, inclusions, partial dissolution and local recrystallization (Fig. 2a); of interest is fact that these features tend to occur mainly along the external limits of the cores. Zoning varies from concentric oscillatory to indistinct. Convolute zoning can be found in most of the metamict grains. The latter are mantled by rims with distinct concentric oscillatory or sector zoning showing little subsolidus alteration features. CL intensities vary towards the outermost zones, increasing or decreasing from grain to grain (Fig. 2a). Overall, zircons from the Papanduva Pluton have CL-dark rims whereas those from the Mandira Pluton exhibit CL-brighter rims. A thin band showing very strong CL contrast appears in some grains between the core and rim zones (Fig. 2b). In particular, most of the grains from sample MAN-13A are surrounded by an irregular thin overgrowth with weak to very weak CL brightness, possibly reflecting post-magmatic, hydrothermal processes.

Trace element composition

Zircon from the peralkaline granites contain low U contents (159 – 428 ppm), Pb (23 – 54 ppm) and Th (219 – 698 ppm), as well as high and variable Hf abundances (5680 – 13431 ppm). Th/U ratios vary from 1.1 to 1.9. The highest Th abundance (XX ppm) is recorded in zircon from the Papanduva pluton, whereas Pb contents are similar and U and Hf contents are higher in the Mandira Pluton.. Consequently, Th/U ratios are higher for zircons from the Papanduva Pluton. Ti contents are variable and high (15 – 187 ppm). Total rare-earth elements (REE) contents vary from 2381 to 5176 ppm, with zircons from the Papanduva Pluton being slightly enriched in light REE (LREE) (up to 593 ppm) relative to those from the Mandira Pluton (up to 494 ppm). Of note, average LREE contents (La to Nd) for granitic zircons are the highest among all analyzed samples.

Fig. 4a illustrates average chondrite-normalized rare-earth element (REE) patterns for zircons from the alkaline association. The patterns for zircon from the Papanduva and Mandira Plutons are quite coherent and show REE concentrations that are 500 to 1,500 times chondrite values. These are characterized by marked enrichment in heavy REEs (HREEs) relative to the

LREEs, with Yb_N/La_N between 19 and 1080, as well as a negative Eu-anomaly, with $\text{Eu}/\text{Eu}^* [\text{Eu}_N/(\text{Sm}_N \cdot \text{Gd}_N)^{1/2}]$ up to 0.09. The relative LREE enrichment results in flatter patterns, with $0.8 < \text{Sm}_N/\text{La}_N < 13$. As a consequence, the positive Ce-anomaly, a common feature of natural zircon (e.g. Hoskin and Schaltegger, 2003), is less apparent in the granitic zircons with $\text{Ce}/\text{Ce}^* [\text{Ce}_N/(\text{La}_N \cdot \text{Pr}_N)^{1/2}]$ up to 22.0.

Figure 4: Chondrite-normalized REE plots for zircon crystals from (a) A-type granites, syenites and rhyolite of the alkaline association and (b) A-type granites of the aluminous association of the Graciosa Province. Plots represent average compositions of selected zircons from the studied samples.

Table 1: Average trace element composition (ppm) of selected zircon crystals from A-type granites, syenites and associated rhyolite of the alkaline association and granites of the aluminous association of the Graciosa Province

Sample	MAN-13A	MR-39	CO-32C	CO-32D	CO-38	MR-254
Analyses	n = 3	n = 4	n = 4	n = 5	n = 4	n = 5
Pluton	Mandira	Papanduva*		Corupá		M. Red. Complex
Rock Type	peralkaline granites			syenites		rhyolite
P	207	483	399	332	74	365
Sc	188	228	203	288	203	298
Ti	74.4	73.8	6.2	7.1	12.2	3.5
Mn	2.3	3.9	1.1	0.7	0.4	0.9
Sr	3.9	2.9	7.3	4.2	0.8	2.3
Y	5606	4895	20890	12018	1890	5411.7
Nb	80.8	80.5	74.1	45.3	36.5	69.9
Mo	28	39	32	37	33	49
Ba	1.1	2.3	0.1	0.2	0.1	0.2
La	16	41	1.0	0.4	0.2	0.8
Ce	139	177	287	154	28	54
Pr	13	19	3.3	2.4	0.5	0.6
Nd	55	97	52	40	7.3	8.6
Sm	28	41	140	68	11	17
Eu	0.5	1.9	7.3	6.8	0.3	0.3
Gd	134	131	824	337	55	106
Tb	48	43	266	102	15	39
Dy	560	558	2943	1285	192	530
Ho	206	192	682	426	62	195
Er	843	819	2446	1847	272	829
Tm	154	124	401	331	53	157
Yb	1245	956	2686	2638	446	1293
Lu	208	165	360	437	83	228
Hf	9498	7093	8832	8162	7099	15264
Ta	7.4	4.9	18	2.5	0.8	5.6
²⁰⁶ Pb	161	146	154	123	19	195
Th	452	464	1768	842	96	1071
U	368	285	407	379	51	523
Zr/Hf	47.5	73.2	53.4	70.9	79.5	41.0
Lu/Hf	0.022	0.024	0.041	0.054	0.012	0.015
Th/U	1.2	1.6	4.3	2.2	1.9	2.1
Y/Ho	27.2	26.9	30.6	28.2	30.8	27.9
REE	3651	3365	11099	7675	1224	3459
LREE	252	375	484	265	47	81
HREE	3399	2990	10616	7410	1177	3378
T(°C)†	883	966	756	748	774	730

Concentrations are in ppm

SiO₂ = 31.6 wt. % was used as internal standard (discussion in text)

*Plutons Papanduva and Quiriri are part of the Morro Redondo Complex

† mean temperatures calculated with the Ti-in-zircon thermometer from selected samples (discussion in text)

Table 1: cont.

Sample	MR-161	MR-186A	MR-201A	AT-15C	GUA-16
Analyses	n = 5	n = 5	n = 2	n = 3	n = 3
Pluton		Quiriri*		Alto Turvo	Guaraú
Rock Type	aluminous granites				
P	919	678	433	731	220
Sc	287	273	244	254	226
Ti	10	15	6.6	16	19
Mn	3.3	2.2	1.1	7.8	13
Sr	2.1	1.8	1.4	3.6	2.3
Y	4055	3739	3148	2674	2890
Nb	53.2	60.7	49.9	52.7	57.3
Mo	35	38	45	46	37
Ba	2.9	3.0	0.1	6.7	3.5
La	1.9	4.5	6.0	28	9.3
Ce	46	57	61	114	43
Pr	0.8	1.7	1.5	11	3.3
Nd	7.8	11	9.8	54	23
Sm	12	13	10	23	29
Eu	0.7	0.9	0.6	1.5	0.6
Gd	67	71	55	72	107
Tb	24	24	20	22	34
Dy	343	312	284	256	338
Ho	135	128	108	87	113
Er	579	556	477	431	494
Tm	123	120	96	93	96
Yb	1075	989	853	884	816
Lu	191	194	169	145	141
Hf	14798	15391	14741	13602	10903
Ta	3.2	3.5	4.7	3.0	2.4
²⁰⁶ Pb	290	157	124	108	91
Th	537	583	522	313	358
U	285	339	336	321	191
Zr/Hf	52.0	48.3	35.7	45.4	44.8
Lu/Hf	0.013	0.013	0.012	0.011	0.013
Th/U	1.8	1.7	1.6	1.0	1.8
Y/Ho	30.9	29.6	29.3	30.6	26.7
REE	2605	2482	2151	2168	2248
LREE	69	87	89	176	108
HREE	2536	2395	2062	1992	2140
T(°C)†	785	821	739	832	856

5.1.2. Syenites

Textures

Zircon from syenites of the Corupá Pluton can be grouped into two morphological groups: (1) Within the oversaturated alkali-feldspar green syenite of sample CO-32C (Fig. 2c) and in the melasyenite of sample CO-32D (Fig. 2d) zircons occur as blocky large grains (> 300 μm diameter) with well-developed {101}-pyramid and weakly developed {110}-prism faces. Many of them are highly fractured and few preserve crystal faces. CL images reveal an incipient to broad banded zoning with weak to moderate CL contrast. Partial dissolution and recrystallization features can be found in some cores. (2) Within the saturated pink alkali-feldspar syenite of sample CO-38 (Fig. 2e), zircons are similar to those found in the peralkaline granites (e.g. Fig. 2a). They are subhedral to euhedral, medium-to-large grains (140 – 300 μm diameter) with well-developed {100} and {101} faces. The cores exhibit indistinct and concentric oscillatory zoning with weak CL contrast (Fig. 2e). Some of them also show embayment due to local reabsorption, as well as fluid inclusions; however, these features are less common than in the peralkaline granites. Rim zones with narrow concentric oscillatory zoning mantle cores. Similar to what is observed in zircon from the peralkaline granites, some cores are conformably mantled by a CL-bright thin band and then overlain by the rim zones.

Trace element composition

Zircon trace element compositions for the metaluminous syenites of the Corupá Pluton are similar for samples CO-32C and CO-32D but differ compared to sample CO-38. The former contain Th/U ratios between 1.1 and 5.8, slightly lower Hf (6799 – 11473 ppm) and Ti (1.8 – 13 ppm) abundances, and higher Th (178 – 2339 ppm), U (167 – 642 ppm), Pb (70 – 199 ppm) and REE (5561 – 13717 ppm) contents relative to those recorded in zircons from the peralkaline granites. Zircon from sample CO-38 are characterized by even lower REE (1114 – 1366 ppm) and Hf (6167 – 8465 ppm) contents, slightly higher Ti (7.8 – 18 ppm) and the lowest Th (61 – 117 ppm), U (43 – 56 ppm) and Pb (17 – 22 ppm) abundances among all analyzed samples. Th/U ratios for this sample vary between 1.4 and 2.2.

REE average patterns for the syenites from the Corupá Pluton are shown in Fig. 4a. The patterns are coherent and typical of those of igneous zircon (Hoskin and Schaltegger, 2003), though somewhat dispersed due to the significant difference in REE contents between the different samples. The patterns illustrated in Fig. 4a are characterized by a strong enrichment in HREEs relative to LREEs, with Yb_N/La_N ratios ranging between 1715 and 17306 for sample CO-32 and from 844 to 11105 for sample CO-38; moreover, positive Ce- and negative Eu-anomalies, with Ce/Ce^* ratio between 18 – 81 and 11 – 42 and Eu/Eu^* ratio between 0.06 – 0.24 and 0.02 – 0.05 are detected for the pair of samples CO-32 and sample CO-38, respectively. The LREE contents are much lower than those recorded in the peralkaline granites, resulting in a steeper pattern with Sm_N/La_N ratios between 146 – 970 and 21 – 294 for samples CO-32 and CO-38, respectively.

5.1.3. Rhyolite

Textures

Zircons from the rhyolite of the Morro Redondo Complex appear as subhedral to euhedral medium grains (130 – 250 μm diameter) sharing morphological similarities with those from the peralkaline granites. They are characterized by weak to very weak CL contrast and show little or no zoning. None of the grains exhibit strong internal discontinuities typically indicative of the presence of inherited components (Fig. 2f).

Trace element compositions

Trace element compositions of rhyolitic zircon from the Morro Redondo Complex (sample MR-254) record the highest Hf (13433 – 17582 ppm) and lowest Ti (1.9 – 6.1 ppm) contents for the alkaline association. These zircons are also marked by lower REE (2798 – 4358 ppm), Th (890 – 1327 ppm), U (445 – 610 ppm) and Pb (171 – 213 ppm) contents. Th/U ratios vary between 1.72 and 2.55.

In Fig. 4a, the average REE pattern for zircons from the rhyolite is shown and compared relative to those for granites and syenites. The measured REE contents are 2 to 1,600 times chondrite, which correspond to enrichment levels similar to those for zircons from the peralkaline granites. However, these REE contents are higher than those recorded in zircons from syenite (sample CO-38), whereas the HREE contents are similar to those from the peralkaline granites. The chondrite-normalized pattern is positive, steeply sloped with Yb_N/La_N values between 1034 and 23305, Sm_N/La_N ratios between 11 and 316, and contains positive Ce- ($11 < \text{Ce}/\text{Ce}^* < 41$) and negative Eu- ($0.01 < \text{Eu}/\text{Eu}^* < 0.03$) anomalies.

5.2. ALUMINOUS ASSOCIATION

Texture

Zircons from the aluminous granites of the Quiriri (samples MR-161, MR-186A and MR-201A), Alto Turvo (AT-15C) and Guaraú (GUA-16) Plutons occur in a variety of forms (Fig. 3). Most of the grains are euhedral, medium-to-large (70 to 300 μm diameter), with moderate developed {110}-prism and well-developed {101}-pyramid faces. The predominance of the prismatic {110} form increases from the Quiriri (Figs. 2a to c) to Alto Turvo (Fig. 2d) and Guaraú Plutons (Fig. 2e). The remainder of the grains are stubby, with moderate to well-developed {100}-prism and weak developed {211}-pyramid faces; the latter are more important in the Quiriri and Alto Turvo Plutons (Figs. 2a–d).

CL images reveal ubiquitous zoning and some complex internal textures. Most grains contain a core with strong CL contrast and simple banding, or indistinct to discrete oscillatory zoning surrounded by rim zones with weak to moderate CL contrast revealing a fine, concentric oscillatory zoning (e.g. Fig. 2d). In a few zircons, the boundary between cores and rims is delineated by a thin band with very strong CL contrast. Partial dissolution, local resorption and recrystallization, as well as inclusions are common features mainly in the inner portions of the grains, especially along the boundary core-rim. These are significant features mainly in the Alto Turvo and Guaraú Plutons

(Figs. 2d–e). In fact, the latter also contains a large number of grains with very weak CL contrast rendering it difficult to distinguish between core and rim zones. The presence of inherited components is also a common feature in grains from these plutons (e.g. Fig. 2e). Most of the cores show weaker CL contrast than the surrounding portions. Likewise, hydrothermal overgrowths with weak to very weak CL contrast and spongy textures are also a characteristic texture of the zircons.

Trace element composition

Zircons from the Quiriri (MR-161, MR-186A and MR-201A), Guaraú (GUA-16) and Alto Turvo (AT-15C) Plutons have compositions marked by lower and variable Th (100 – 795 ppm) and U (54 – 432 ppm) contents, and higher and variable Pb (26 – 818 ppm), Hf (9021 – 17772 ppm) and Ti (5.8 – 26 ppm) abundances relative to the granitic rocks from the alkaline association. Th/U ratios range between 0.93 and 2.19. REE contents are also invariably lower (1266 – 3803 ppm) and can be successfully used to distinguish zircons from alkaline and aluminous associations. Major chemical differences between the zircons for the plutons investigated here from the aluminous association are mainly related to their LREE contents. The latter are on average much higher in the Alto Turvo Pluton (60 – 321 ppm) followed by the Guaraú Pluton (61 – 166 ppm) and then the Quiriri Pluton (47 – 110 ppm).

Chondrite-normalized REE average patterns for zircons from the aluminous granites are shown in Fig. 4b. The measured REE concentrations are 4 to 1,600 times chondrite characterized by positive slopes (Yb_N/La_N between 23 and 3113) and negative Eu-anomalies ($0.01 < Eu/Eu^* < 0.18$). Some distinction can be made in the patterns for the LREE. The higher LREE contents recorded for zircons from the Guaraú and Alto Turvo Plutons result in flatter patterns with Sm_N/La_N ratios between 1 and 32, and less pronounced positive Ce-anomaly ($1 < Ce/Ce^* < 8$), especially for the Guaraú Pluton. In contrast, LREE patterns for the Quiriri Pluton are slightly more fractionated, with $2 < Sm_N/La_N < 41$ and indicate a more pronounced positive Ce-anomaly ($3 < Ce/Ce^* < 35$).

In general, trace element contents correlate with the CL intensities for different crystal zones in all analyzed samples. In most cases, zones characterized by high CL contrast, primarily intermediate and core zones in the aluminous granites and intermediate and rim zones in the peralkaline granites and syenites, correspond to high Nb, Hf and Zr contents. Conversely, zones with low CL contrast, mainly crystal cores in the peralkaline granites and syenites and rims in the aluminous granites are characterized by high Th, U and Pb contents. Ti and REE contents are variable. Of note, the relationship between CL intensity variations and crystal morphological positions (core, rim and intermediate position) is not always straightforward.

6. Ti-IN-ZIRCON THERMOMETRY

In order to obtain an estimate of the zircon crystallization temperatures, Ti abundances (Table 1) were applied using the geothermometer of Watson et al. (2006) and Watson and Harrison (2005) and its recalibrated version (Ferry and Watson, 2007). The geothermometer of Watson et al. (2006) underestimated temperatures compared to available Zr-saturation temperatures for these rocks. In contrast, Ferry and Watson (2007) considers the $a\text{TiO}_2$ and $a\text{SiO}_2$ at the time of zircon crystallization and yielded more reliable and realistic temperatures. Qualitative values for $a\text{TiO}_2$ and $a\text{SiO}_2$ activities were adopted and based mainly on textural and mineralogical observations and comparable data from the literature. Given the evolved nature of the magmas involved and the ubiquitous nature of quartz in most of the samples investigated here the $a\text{SiO}_2$ was fixed at 1 (Watson et al., 2006; Clairbone et al., 2010). The exceptions are samples CO-32D and CO-38, which represent saturated alkali-feldspar syenites from the Corupá Pluton, where $a\text{SiO}_2 = 0.8$ was used. The presence of coexisting Ti-bearing phases, such as titanite and ilmenite mainly in the aluminous granites indicate that $a\text{TiO}_2$ was sufficiently high. Based on the work by Clairbone et al. (2010), the $a\text{TiO}_2$ was fixed at 0.5 for the peralkaline granites and rhyolite, 0.6 for syenites, and 0.7 for the aluminous granites. The calculated temperatures seem to agree well with field, petrologic and geochemical evidences, with the exception of calculated temperatures for zircons from the

peralkaline granites from the Papanduva and Mandira Plutons. The high temperatures recorded for the latter and to a lesser extent for zircons from the Alto Turvo and Guaraú Plutons are linked to high Ti concentrations; these may be attributed to the presence of Ti-bearing inclusions, or related to late-stage fluid interaction (see discussion below). Thus, the reliability of these data is doubtful.

Granitic and syenitic rocks from the alkaline association define a broad range of calculated Ti-zircon temperatures from 725 to 978 °C. The calculated mean temperatures for zircons from the Mandira and Papanduva Plutons are 883 ± 13 °C and 966 ± 8 °C, respectively (Table 1). Zircons from the latter yield higher temperatures ($\sim 955 - 978$ °C) whereas those from the former, give calculated temperatures less than ~ 900 °C (Fig. 5). Conversely, temperatures calculated for zircons from the syenites of the Corupá Pluton are lower and variable. Mean temperatures vary from 748 ± 23 °C and 756 ± 15 °C for samples CO-32D and CO-32C, respectively, and 774 ± 13 °C for sample CO-38 (Table 1). A broad distribution of temperatures is recorded for sample CO-32D (between 683 and 804 °C), while in samples CO-32C and CO-38 temperatures define a more restricted interval between 725 – 789 °C and 749 – 802 °C, respectively (Fig. 5). Lastly, temperatures calculated for zircons from the rhyolite range from 696 to 765 °C with a mean value of 730 ± 16 °C (Table 1, Fig. 5).

Granites from the aluminous association show a fairly restricted temperature variation, ranging from 729 to 884 °C. The highest temperatures are calculated for zircons from the Alto Turvo and Guaraú Plutons with mean values of 832 ± 6 °C and 856 ± 20 °C, respectively; whereas zircons from the Quiriri Pluton exhibit mean temperatures between 739 ± 8 °C and 821 ± 9 °C (Table 1, Fig. 5). The higher temperatures for this pluton ($\sim 787 - 847$ °C) are calculated from sample MR-186A (Fig. 5).

Ferry and Watson (2007) and Ferriss et al. (2008) suggest a moderate pressure dependence of the Ti-zircon geothermometer corresponding to $\sim 5 - 10$ °C/kbar. Given that the Ferry and Watson (2007) thermometer is calibrated at 10 kbar, the calculated temperatures reported here can be either tens of degrees too high (shallow crust) or too low (deep crust or upper mantle).

Considering the fact that the magmas giving rise to the Graciosa Province were emplaced at shallow crustal levels (ca. 1 – 2 Kbar, Gualda and Vlach, 2007a), our calculated temperatures may be systematically overestimated. Nevertheless, it seems unlikely that the calculated temperatures reported here are not significant, at least for the syenites, aluminous granites and the rhyolite. These represent reasonable magmatic temperatures, and in most cases are similar to the calculated Zr-saturation temperatures, even with a downward correction (see Clairbone et al., 2010).

Figure 5: Diagram showing the temperatures of zircon crystallization calculated with the Ti-in-zircon thermometer of Watson and Harrison (2005) and Watson et al. (2006) for selected crystals from the studied samples.

7. LA-ICP-MS U-Pb DATING RESULTS

7.1. ALKALINE ASSOCIATION

7.1.1. Granites

A total of 25 representative zircons from the peralkaline granites of Papanduva and Mandira Plutons were analyzed for their U-Pb isotopic compositions and these are listed in Table 2. For the Papanduva Pluton, three analyses associated with degrees of discordance <4% yield a Concordia age of 580 ± 8 Ma, identical to the weighted mean (WM) $^{206}\text{U}/^{238}\text{Pb}$ age at 582 ± 5 Ma obtained from

19 spots and interpreted as the best estimate for the crystallization age. Furthermore, eight analyses from crystal cores and rims define a distinct and younger WM $^{206}\text{Pb}/^{238}\text{U}$ age of 562 ± 7 Ma (Fig. 6a). For the Mandira Pluton, a WM $^{206}\text{U}/^{238}\text{Pb}$ age of 567 ± 6 Ma is obtained from ten spots (Fig. 6b), which is similar to the younger age population recorded in the Papanduva Pluton (Fig. 6a).

7.1.2. *Syenites*

A set of 46 zircons from the Corupá Pluton syenites were investigated and selected analyses are shown in Table 2. The entire data set is available as supplementary material. Six analyses for the pink syenite (sample CO-38) that are associated with degrees of discordance $<10\%$ yield a Concordia age of 586 ± 8 Ma (Fig. 6c). This result is identical to the WM $^{206}\text{Pb}/^{238}\text{U}$ age of 586 ± 7 Ma based on from 11 analyses (Fig. 6c), which represents the best estimate for the emplacement age since the discordance associated with the Concordia age is relatively high. Moreover, a set of 14 analyses from cores and rims also yield a younger WM $^{206}\text{Pb}/^{238}\text{U}$ age of 566 ± 6 Ma (Fig. 6c), which is similar to that recorded for the younger ages from the Papanduva peralkaline granites (Fig. 6a, b). Ten analyses with degrees of discordance $<5\%$ for the green syenite (sample CO-32C) give a Concordia age of 583 ± 6 Ma, which is identical to the WM $^{206}\text{Pb}/^{238}\text{U}$ age of 582 ± 5 Ma obtained from 19 analyses (Fig. 6d). Ten analyses for the melasyenite (sample CO-32D) with degrees of discordance $<6\%$ yield a Concordia age of 580 ± 6 Ma, which is identical (given associated uncertainties) to the WM $^{206}\text{Pb}/^{238}\text{U}$ age (582 ± 5 Ma; Fig. 6d).

7.1.3. *Rhyolite*

The rhyolite from the Morro Redondo Complex was dated using a set of 20 zircon crystals and selected analyses are listed in Table 2. The entire date set is available as supplementary material. Eleven analyses taken in cores and rims and associated with degrees of discordance $<10\%$ yield a Concordia age of 585 ± 5 Ma, which is identical to the WM $^{206}\text{Pb}/^{238}\text{U}$ age at 585 ± 6 Ma based on 16 analyses (Fig. 6f).

7.2. ALUMINOUS ASSOCIATION

A total of 83 zircons representative of those associated with the aluminous granites from the Quiriri (48 crystals), Guaraú (17 crystals) and Alto Turvo (18 crystals) Plutons were analyzed. Results are summarized in Table 3 and in the Concordia diagrams of Fig. 7. Zircons for several of the biotite granite samples from the Quiriri Pluton investigated here yield the same age. Seven analyses from sample MR-161 with associated degrees of discordance <6% result in a Concordia age of 584 ± 7 Ma, which is identical to the WM $^{206}\text{Pb}/^{238}\text{U}$ age at 586 ± 5 Ma based on 15 analyses (Fig. 7a). Sample MR-186A yields a Concordia age of 584 ± 7 Ma based on seven analyses with associated degrees of discordance <5%, and is similar to the WM $^{206}\text{Pb}/^{238}\text{U}$ age at 584 ± 4 Ma using 20 analyses (Fig. 7b). Seven analyses with associated degrees of discordance <4% for sample MR-201A give a Concordia age of 583 ± 7 Ma, similar to the WM $^{206}\text{Pb}/^{238}\text{U}$ age at 583 ± 6 Ma based on 14 spots (Fig. 7c).

The granites from the Alto Turvo Pluton record slightly older ages but also exhibit larger associated degrees of discordance. A set of four analyses with associated degrees of discordance <8% yield a Concordia age of 593 ± 9 Ma, and is similar to the WM $^{206}\text{Pb}/^{238}\text{U}$ age of 596 ± 7 Ma based on 8 spots (Fig. 7d).

For the Guaraú Pluton, the best estimate for the time of emplacement is based on the WM $^{206}\text{Pb}/^{238}\text{U}$ ages and seven analyses yield an age of 585 ± 10 Ma (Fig. 7e). A concordant crystallization age was not obtained due to the frequent presence of inherited components, mainly in the cores. Analysis of one core yielded a concordant age of 2.97 ± 0.034 Ga (Fig. 7f).

A younger WM $^{206}\text{Pb}/^{238}\text{U}$ age population is recorded in several crystal cores and rims in all samples from the Quiriri and Alto Turvo Plutons. The ages cluster between 563 ± 9 Ma and 565 ± 5 Ma for the Quiriri Pluton (samples MR-161 and MR-186A, respectively) and 572 ± 8 Ma in the Alto Turvo Pluton (Figs. 7a–d). Of note, a few analyses for zircons from the Guaraú Pluton yield younger ages at ca. 561 Ma, which is the same age as that defined by the lower intercept in Fig. 7f. These ages are associated with large degrees of discordance and were therefore omitted.

Figure 6: Concordia diagrams for the studied samples of the alkaline association of the A-type Graciosa Province showing the calculated Concordia Age and correspondent weighted mean (WM) $^{206}\text{U}/^{238}\text{Pb}$ age. In (a) (sample MR-39) and (c) (sample CO-38), the calculated (WM) $^{206}\text{U}/^{238}\text{Pb}$ age for a younger age population is also presented. Data-point error ellipses are 2σ . Discordant analyses were omitted from the diagrams.

Figure 7: Concordia diagrams for the studied samples of the aluminous association of the A-type Graciosa Province showing the calculated Concordia Age and correspondent weighted mean (WM) $^{206}\text{U}/^{238}\text{Pb}$ age. The WM $^{206}\text{U}/^{238}\text{Pb}$ age calculated for a younger age population in most of the samples is also presented, as well as the age of an inherited core from sample GUA-16 (f). Data-point error ellipses are 2σ . Discordant analyses were omitted from the diagrams.

8. DISCUSSION

8.1. GEOCHRONOLOGICAL OVERVIEW

A critical review of the available geochronological data for the Graciosa Province is presented by Vlach et al. (2011). This study considers more than 30 reliable age determinations obtained by the K-Ar (biotite and amphibole), Rb-Sr (whole-rocks) and U-Pb (ID-TIMS, SHRIMP) isotopic systems that yielded weighted averages of 576 ± 26 Ma, 580 ± 20 Ma and 581 ± 16 Ma, respectively. Moreover, the variation in ages observed for individual plutons are comparable with those observed for the entire data set compiled by the authors. If the newly acquired in-situ U-Pb LA-ICP-MS age determinations obtained by Braun et al. (2010), Koch et al. (2011) and Vlach et al. (2012), and the ID-TIMS results of Vlach et al. (2011) are included in the compilation, then a better constrained average U-Pb age of 583 ± 6 Ma is obtained for the whole magmatism that formed the province. As pointed out by Vlach et al. (2011), the good agreement achieved amongst the three chronometers employed is consistent with magma emplacement at shallow levels (Hallinan et al., 1993; Gualda and Vlach, 2007a), and hence associated with relatively fast cooling rates and closure of the K-Ar system not long after final crystallization.

The age determinations reported here are in good agreement with the previous data. The older age (593 ± 9 Ma) obtained for the Alto Turvo Pluton is similar to those obtained by Siga Jr. (unpublished data) for granitic rocks and Vlach et al. (2012) for syenitic rocks from the pluton at 593 ± 34 (ID-TIMS) and 595 ± 8 Ma (LA-ICP-MS), respectively. This suggests that its emplacement occurred slightly prior to the main magmatic episode within the province. Conversely, the age obtained for the peralkaline granites of the Mandira Pluton (ca. 567 Ma), though younger, overlaps (given the associated uncertainties) with the weighted average age of 577 ± 9 Ma obtained by Koch et al. (2011). However, the latter age is associated with a high MSWD value (6.0) and low probability of concordance (0.0), and careful inspection of these data reveals a significant age population around 560 – 570 Ma. Moreover, that work also presents an age of 561 ± 6 Ma based on 41% of the data, with a relative Misfit of 0.72 obtained with the age deconvolution method of

Sambridge and Compston (1994). Thus, the age of 567 ± 6 Ma reported here represents the best estimate for the emplacement of the peralkaline granites of the Mandira Pluton. Of interest, the granites from the aluminous association within this pluton were dated at 584 ± 4 Ma (Koch et al., 2011).

The emplacement age for the rhyolite from the Morro Redondo Complex obtained here (ca. 585 Ma) agrees well with the available age determinations (between 570 and 598 Ma) for felsic volcanic rocks that appear in the Campo Alegre and Guaratubinha volcano-sedimentary basins associated with the Graciosa Province (Siga Jr. et al., 1997; 1999; Basei et al., 1998; Cordani et al., 2000).

8.2. UNDERSTANDING THE YOUNGER AGE POPULATION

An interesting result of this work is the identification of a population of zircons clearly younger than the 580 – 586 Ma ages usually considered as best estimates for the crystallization of the Graciosa Province plutons (e.g. Vlach et al., 2011). Both weighted mean $^{206}\text{Pb}/^{238}\text{U}$ and several concordant ages of ~565 Ma are recorded in many zircons from the Papanduva, Quiriri and Corupá Plutons, at a minimum confidence level of 81% and 85% for the peralkaline granites of the Papanduva Pluton and the metaluminous pink syenites of the Corupá Pluton, respectively; 95% confidence level for the metaluminous to slightly peraluminous granites of the Quiriri Pluton. In the Alto Turvo Pluton, a younger age population at ca. 572 Ma for a minimum confidence level of 89% is present. With regards to the Guaraú Pluton, despite the high associated uncertainties and the small number of analyses, it is also possible to recognize a younger age population at 561 ± 12 Ma, similar to the age obtained for the lower intercept in Fig. 7f (561 ± 22 Ma). Moreover, these younger ages are similar to that obtained here for the peralkaline granites of the Mandira Pluton (Fig. 6b).

There are two possible explanations for the systematic presence of the ~565 Ma old zircons for the various plutons: 1) It represents a distinct age population that reflects a separate crystallization period; 2) The younger aged zircons may reflect late- to post-magmatic/hydrothermal

fluid-induced alterations. It is also possible that the younger ages are the result of a recent Pb loss event. In order to test this hypothesis, a comparison of textures and trace element compositions can be made between zircons (or crystal zones) yielding younger ages and those dated at 580 – 586 Ma, and with zircons representing a distinct, clearly hydrothermal-altered population from the Mandira Pluton, which yield no reliable ages. From a textural point of view, younger ages are obtained from both rims and cores and a direct relationship between ages and evidences of hydrothermal alteration and/or metamictization, such as dissolution, spongy textures, fractures and pores is not straightforward; this is especially true for zircons from the syenites and aluminous granites. In most cases, younger ages are recorded in pristine crystals with well-defined compositional zoning (e.g. Figs. 2e, 3b–d). Similarly, the relationship between CL emission intensity and ages is somewhat complex. Essentially for the Corupá and Quiriri Plutons, many zircons exhibit core-to-rim textural variations that correspond to a decreasing trend in ages. An excellent example of this is illustrated in Figure 8, which shows a typical zircon crystal from the metaluminous, saturated, pink-colored alkali-feldspar syenite from the Corupá Pluton (sample CO-38). The core is older with an absolute $^{206}\text{Pb}/^{238}\text{U}$ age of 585 Ma and corresponds to a low CL contrast, suggesting low Th, U and Pb contents. The external core zone shows strong resorption and embayment and the occurrence of a thin layer with high CL contrast; minor inclusions with no or very low CL contrast also occur. The core is mantled by an intermediate zone yielding an absolute age of 579 Ma. This zone is characterized by an increase in the CL contrast and the presence of a well-defined oscillatory compositional zoning. Albeit resorption features are less evident than those found in the external core area, the interface between intermediate and rim zones is defined by the presence of a very thin high-CL band. Lastly, the rim zone records a younger absolute age of 565 Ma, and is characterized by the absence of compositional zoning. Clairbone et al. (2010) describe similar textures in zircons from the Spirit Mountain Batholith (USA), although these lack a core-to-rim geochronological control. This feature suggests zircon crystallization in a complex magmatic environment with fluctuating conditions, or represents separate, repeated episodes of crystallization. In such a scenario, resorption surfaces and embayments indicate repeated episodes of Zr-saturated magma rejuvenation, or possibly mixing with hotter, Zr-undersaturated magmas. Clairbone et al.

(2010) also identify thin bright (high CL) zones between the different crystal zones. The latter yield higher calculated Ti-zircon temperatures (T_{Tiz}), suggesting that the supposed rejuvenation or magma mixing episodes occurred at a higher temperature.

Figure 8: Cathodoluminescence (CL) image of a typical zircon crystal from sample CO-38 showing textural variation from core to rim accompanied by a decreasing in absolute $^{206}\text{U}/^{238}\text{Pb}$ age (2σ error). Scale bar = 200 μm

A comparison of the trace element composition for crystal areas yielding older (ca. 580 – 586 Ma) and younger (ca. 565 Ma) ages in the Corupá and Quiriri Plutons is presented in the diagrams of Fig.9. Overall, the main chemical variations are related to a discrete increasing of Hf abundances (Fig. 9a) and increasing intensity of the positive Ce anomaly (Ce^* parameter; Fig. 9d), and positive correlations between Th, U, Pb and REE abundances and increase in ages (Figs. 9b–c). Ti abundances are also lower in the zircon zones characterized by younger ages, which in turn yield low calculated T_{Tiz} .

For the peralkaline granites, although many crystal cores yield younger ages (ca. 565 – 575 Ma) and are mantled by younger rims (≤ 563 Ma), it is not uncommon to find younger cores surrounded by older (> 580 Ma) rims. Zircons from these rocks, especially from the Papanduva Pluton, record more clearly textures indicative of complex crystallization environments and/or transformation features, such as resorption and recrystallization surfaces, embayment, convolute zoning and associated inclusions. The observed chemical variations shown in Figure 9 strongly contrast with those described for the syenites and aluminous granites. They are characterized by a

remarkable increasing of the Nb+Ta contents from the older crystal zones (59 – 71 ppm) to the younger ones (91 – 120 ppm) (Fig. 9a), as well as significant increasing of Th and U and REE (primarily LREE) abundances towards younger ages (Figs. 9b–c). Ti abundances (not shown in Fig. 9) follow these elements, yielding higher calculated T_{TiZ} for the younger age zones. Conversely, the positive Ce anomaly increases towards the younger ages, similarly to the observed in the syenites and aluminous granites (Fig. 9d).

The textures and chemical variations observed in the zircons from the peralkaline granites, as well as their distinct LREE-enriched pattern suggest interaction with late-stage to post-magmatic/hydrothermal fluids (e.g. Hoskin and Schaltegger, 2003). This is best exemplified by the trace element compositions for a population of zircons from the Mandira Pluton (sample MAN-13A), which exhibit well-marked late-to post-magmatic/hydrothermal evidences, including spongy texture (cf. Corfu et al., 2003, Hoskin and Schaltegger, 2003; Fig. 10). Trace element abundances are presented in Figs. 11 and 12 and indicate the existence of two types of late-stage to post-magmatic/hydrothermal alteration, here referred to as hydrothermal zircon type-1 and type-2. Type-1 zircons were subjected to a smaller degree of hydrothermal alteration since it is still possible to distinguish between cores and rims (and an incipient magmatic zoning), which are strongly enriched in REE, Th, U and Pb (Fig. 11). In contrast, type-2 hydrothermal zircons are strongly altered and typically exhibit ‘spongy’ texture, and exhibit relatively depleted trace element compositions and REE patterns (Fig. 12a); however, of interest these contain similar compositions and patterns compared to relatively well preserved zircons yielding the typical “Graciosa Province” age (~585 Ma), in particular in relation to the REE, Th, U and Pb abundances (Figs. 11 and 12a). The geochemical nature of hydrothermal zircon type-2 is also similar to the LREE-enriched zircons from the Alto Turvo and Guaraú Plutons (Fig. 12b). In fact, many zircons from these plutons show hydrothermal features similar to those described for the peralkaline granites characterized by younger ages around 572 – 561 Ma and generally associated with more altered crystal zones. Of importance, the trace element compositions for the hydrothermal zircons are distinct compared to

those from the syenites and aluminous granites, which exhibit typical igneous patterns (e.g. Hoskin and Schaltegger, 2003).

Figure 9: Diagrams showing trace elements chemical variations and contrasts between zircon crystals and crystal portions yielding ages around 580 – 586 Ma (grey colors) and younger ages at ca. 565 Ma (black colors). Circles: peralkaline granites; stars: syenites; squares: aluminous granites.

The LA-ICP-MS age determinations obtained by Braun et al. (2010) for zircons from aluminous granites of the Serra da Graciosa region (Fig. 1) yield crystallization ages of 581 Ma and younger ages at 539 Ma; the latter are recorded in crystal rims that have suffered late-stage to post-magmatic/hydrothermal transformations. High contents of REEs and HFSEs, such as Nb and Hf as well as Th and U, are characteristic of the rims and analogous to the zircons from the peralkaline granites investigated here. Zircon is highly susceptible to alteration by F-rich residual fluids (e.g. Breiter et al., 2006; Kusiak et al., 2009), which are commonly associated with the evolution of A-type

and alkaline magmas (e.g. Salvi and Williams-Jones, 1996; 2006; Salvi et al., 2000). The circulation of F- and HFSE-rich residual, magmatic fluids under oxidizing conditions leading to the formation of new minerals (e.g., allanite), or promoting intense mineral re-equilibration (e.g., chevkinite) is a well-known phenomenon within the province (Vlach and Gualda, 2007). Similarly, Vilalva and Vlach (2010) argued that the crystallization of turkestanite, a rare Th- and REE-bearing cyclosilicate from the Papanduva Pluton, is also attributed to these late stage processes, which are associated with increases in the abundances of Th, U and REEs. For example, the magnitude of the positive Ce anomaly correlates with an increase in the Sm/La_N values with decreasing age of the zircons investigated here (Fig. 9d). A similar temporal variation is also presented by Ballard et al. (2002) for zircons from barren and Cu-mineralized intrusive rocks from Chile, and interpreted to reflect a systematic increase in the level of oxidation with progressive time of crystallization. Similar correlations are also recorded for the zircons from the syenites and aluminous granites investigated here.

Figure 10: Cathodoluminescence (CL) images of typical zircon crystals from the peralkaline granite of the Mandira Pluton (sample MAN-13A) showing the effects of late- to post-magmatic/hydrothermal fluid interaction.

Figure 11: Chondrite-normalized spider diagrams for selected zircons from the studied samples yielding older (580 – 585 Ma) and younger ages (ca. 565 Ma) compared to the concentrations registered for the hydrothermal zircons from the Mandira Pluton (sample MAN-13A). Note the similar pattern between the studied zircons from the peralkaline granites and the pattern of the hydrothermal zircon type-2. Plots represent average compositions of selected zircons from the studied samples.

Based on these evidences, we suggest that the younger ages at ca. 565 Ma defined by the peralkaline granites, in particular from the Papanduva Pluton, as well as the aluminous granites from the Guaraú and Alto Turvo plutons are attributed to a late-stage to post-magmatic/hydrothermal alteration episode (e.g. Belousova et al., 2002; Hoskin, 2005) under oxidizing conditions. On the other hand, although the younger ages registered for the syenites and aluminous granites from the Corupá and Quiriri Plutons, respectively, can also be related to the same hydrothermal event, the relationship between ages and textural core-to-rim variations observed in many crystals from these rocks (e.g. Figs. 2e and 8) and their contrasting trace element compositions suggest origins from distinct geological events. Coleman et al. (2004) and Miller et al. (2007) argue that younger ages for zircons from the Tuolumme and Mt. Stuart Batholiths (USA) reflect the crystallization age of the last zircons formed in a complex magmatic history. The latter involved successive, temporally distinct magma pulses that had little, if any interaction, over a

period up to 10 Ma. Alternatively, Matzel et al. (2011) estimate a short interval of ca. 5.5 Ma for the formation of the Mt. Stuart Batholith. Hence, it is possible ~565 Ma ages for zircons from the Corupá and Quiriri Plutons may represent final crystallization stages in a protracted magmatic history involving successive magma pulses. The common occurrence of felsic enclaves of monzogranitic composition in the Quiriri Pluton can therefore be interpreted as evidence for multiple pulses of granitic magma. This interpretation implies that the 580 – 585 Ma period represents the emplacement ages of granites and syenites of the Graciosa Province rather than their final crystallization episodes, which occurred at ca. 565 Ma.

The age determinations reported here (and associated errors) indicate that emplacement, petrogenetic evolution and crystallization of the granitic and syenitic magmatism associated with the Graciosa Province spanned 4 to 10 Ma (Figs. 6 and 7). This interpretation is in agreement with the results of Vlach et al. (2011), which suggest an interval no longer than 8 Ma for the entire magmatic history for the province (see also Coleman et al., 2004; Miller et al., 2007). Moreover, the increasing magnitude of the positive Ce anomaly with decreasing age most probably reflects crystallization under progressively more oxidizing conditions. This same conclusion was proposed by Gualda and Vlach (2007c) based on chemical evolution of amphiboles for granites from the Serra da Graciosa region. Assuming a protracted magmatic history for these plutons, the last pulses of melt to enter the plutonic edifices would be more oxidized than their predecessors. Given this scenario, the late-stage to post-magmatic alteration events that overprinted many zircons, mainly from the peralkaline granites, can be attributed to late-stage residual, oxidizing fluids.

Figure 12: Chondrite-normalized REE patterns for (a) selected zircons from the studied samples yielding older (580 – 585 Ma) and younger ages (ca. 565 Ma) compared to the concentrations registered for the hydrothermal zircons from the Mandira Pluton (sample MAN-13A) and (b) samples AT-15C and GUA-16, compared to the hydrothermal zircons. Symbols as in Fig. 11. Plots represent average compositions.

8.3. GEOTECTONIC IMPLICATIONS

Well established tectonic models for southeastern South America are based mainly on the assumption that the geological evolution for the area records the last collisional episodes of the Brasiliano – Pan-African Orogeny (e.g. Basei et al., 2000; Campos Neto, 2000; Heilbron et al., 2004; Basei et al., 2009). The mosaic of blocks that comprise the region (Fig. 1) is believed to have consolidated between 630 – 600 Ma, when several magmatic arcs were active; those represented

by the high-K calc-alkaline Piên-Mandirituba Suite between the Curitiba and Luis Alves Microplate (Fig. 1) and the late-collisional Morro Inglês, Rio do Poço and Canavieiras-Estrela Suites in the Paranaguá Terrain (e.g. Brito Neves et al., 1999; Basei et al., 2005, 2008, 2009). Recent U-Pb geochronological data obtained for these rocks (Harara, unpublished data; Harara et al., 2002; Cury et al., 2008) point to an interval for emplacement and crystallization between 590 and 615 Ma, suggesting a slightly younger age for the amalgamation of these blocks ~590 Ma (Vlach et al., 2011). Hence, the A-type granitoids and associated rocks of the Graciosa Province and the contemporaneous volcano-sedimentary basins in the region formed under an extensional regime during a post-collisional stage (*sensu* Liegeois, 1998) subsequent the final amalgamation of the Luis Alves, Curitiba and Paranaguá terrains (Basei et al., 2009; Vlach et al., 2011).

Alternatively, Almeida et al. (2010, 2012) reviewed the tectonics involved in the formation of the contemporaneous volcano-sedimentary basins in the region and. These authors argued that these basins did not form due to extensional collapse of a thickened crust related to the main collisional episode of the Brasiliano – Pan-African Orogeny that had taken place at ca. 20 – 30 Ma before. Conversely, Almeida et al. (2010, 2012) proposed a model involving extensional stresses caused by mantle thermal anomalies, which were repeatedly interrupted by compressional events causing strike-slip deformation; the latter was possibly related to the far-field response to the latest collisions at the boundaries of the developing Gondwana Plate. Moreover, Almeida et al. (2010) emphasize that the occurrence of basic, intermediate and acid volcanic rocks in these basins coeval with the voluminous Graciosa Province A-type magmatism is indicative of mantle and crustal fusion simultaneous with basin-forming extension.

The geochronological data reported here concur with previous age determinations and interpretations (e.g. Kaul and Cordani, 2000; Basei et al., 2009; Vlach et al., 2011) and indicate that the magmas giving rise to the Graciosa Province granitic and syenitic plutons were emplaced in a post-collisional extensional regime. This occurred mainly between 580 and 585 Ma, a few million years subsequent the late-collisional magmatism. According to Almeida et al., (2012), the extensional stresses in southeastern South America at that time persisted until ca. 535 Ma. In

addition, Basei et al. (2008) suggest a period of ca. 15 Ma for the development of the contemporaneous Itajaí volcano-sedimentary Basin. This despite the compressional regime that culminated with acidic volcanism at ca. 565 Ma. Of note, the sediments of this basin are intruded by the Subida granite of alkaline affinity at ca. 529 Ma (Basei et al., 2008).

In such a geotectonic scenario, the slightly older age obtained here for the Alto Turvo Pluton is compatible with its emplacement in a late- to post-collisional stage prior to the major magmatic activity in the province. Furthermore, Vogado (unpublished data) interprets the geochemical characteristics of this pluton as being transitional between typical Caledonian I-type and A-type granites.

As a final remark, worth to mention that our results corroborate the synchronicity between the Graciosa and Itu A-type Provinces, the latter located to the north of the area, within the Apiaí-Guaxupé Terrain (e.g. Janasi et al., 2009), as pointed out by Vlach et al. (2011).

9. CONCLUSIONS

The generation and evolution of A-type magmas is still a subject of much debate (e.g. Frost and Frost, 2011). The diversity of “granitic” rocks grouped under the A-type label, including peralkaline, metaluminous and even peraluminous varieties renders it difficult to establish a common geological model for the generation of these rocks. Unique crustal or mantle sources (or a mixture of both) have been invoked in proposed models, however, it seems most likely that a variety of source rocks and processes are involved in their generation (Whalen, 2005; Martin, 2006; Bonin, 2007). However, the association of these rocks with post-collisional to anorogenic geodynamic settings under extensional regimes is well established (Martin, 2006; Bonin, 2007; Barbarin, 2011). The geochronological data reported here agree with available radiometric ages and confirm the emplacement of the A-type granitic and syenitic plutons of the Graciosa Province between 580 and 585 Ma. Emplacement of the plutons occurred in an extensional environment related to the geodynamic evolution of the continental blocks that formed the south-southeastern part of the

Gondwana supercontinent at that time. There is insufficient evidence to support systemic migration of the magmatic foci over a long period of time in the Graciosa Province (Vlach et al., 2011).

We report here ages for granitoids from the aluminous (Quiriri, Guaraú and Alto Turvo Plutons) and alkaline associations (Papanduva, Mandira and Corupá Plutons) of A-type granites and syenites within the Graciosa Province. Although the majority of the ages for both associations overlap given their associated uncertainties, average $^{206}\text{U}/^{238}\text{Pb}$ ages based on the whole dataset yield 586 ± 3 , 582 ± 5 and 581 ± 3 Ma for the aluminous granites, peralkaline granites and rhyolite, respectively (not including the 567 Ma Mandira Pluton, and syenites). This result suggests that rocks belonging to the aluminous association may have been emplaced slightly prior to that of their alkaline counterparts. Albeit a discussion about source rocks and genetic processes involved in the formation of the Graciosa Province is beyond the scope of this paper, this will be discussed in a future paper. $\delta^{18}\text{O}$ isotope values and in-situ Hf isotopic data obtained for zircons from the plutons investigated here are consistent with the emplacement sequence cited above.

As pointed out by Vlach et al. (2011) it seems unlikely that magmatism within the Graciosa Province spanned more than a few millions years. The authors estimate a short interval of time around 580 – 583 (± 3) Ma for the emplacement and crystallization of the various plutons. The ubiquitous occurrence of a younger-aged zircon population at ca. 565 Ma, though probably representing an episode of late- to post-magmatic/hydrothermal alteration in the peralkaline granites, suggests a protracted magmatic history for the Graciosa Province, in particular for the syenitic and the aluminous granitic plutons. This implies that magmatism occurred over a slightly longer period of time than the 4 to 10 Myr interval suggested by Vlach et al. (2011).

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ANEXO:

C

**CHEMICAL EVOLUTION (MAJOR AND TRACE ELEMENTS) AND OXYGEN ISOTOPE RATIOS
OF AMPHIBOLES AND CLINOPYROXENES FROM A-TYPE GRANITES OF THE PAPANDUVA
PLUTON, GRACIOSA PROVINCE, S BRAZIL: INSIGHTS INTO THE LATE- TO POST-
MAGMATIC EVOLUTION OF PERALKALINE MELTS AND FLUIDS**

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ABSTRACT

Clinopyroxenes and amphiboles are important mafic minerals in the peralkaline A-type granites of the Papanduva Pluton, Morro Redondo Complex, one of the most important granitic bodies within the Graciosa A-type Province, S-SE Brazil. Clinopyroxenes appear as four distinct textural generations that crystallize during late-magmatic and post-magmatic stages. Magmatic types are aegirine and appear as isolated crystals or in fibrous aggregates with yellow to green colors. Late- to post-magmatic aegirine is characterized by orange colors, whereas post-magmatic types include aegirine crystals mantling primary amphiboles and dark-green aegirine-augite. Amphiboles form isolated interstitial crystals, with green to blue colors, as well as aggregates and porphyroclasts in deformed rock types. They include predominant magmatic ferrichterite and arfvedsonite, as well as restricted post-magmatic riebeckite. Major and trace-element compositions obtained by EPMA and LA-ICP-MS reveal evolutionary trends characterized by increasing Fe³⁺ and Na and decreasing Fe²⁺, Ca, HFSE and REE contents from core to crystal rims, suggesting progressively more oxidizing and peralkaline crystallization conditions. Trace element partition seems to be mainly related to the composition of the coexisting melts or fluid phases. These are typically alkali- and F-rich, show moderate $\delta^{18}\text{O}$ values and higher HFSE and REE contents. Oxygen stable isotope ratios for these minerals are fairly similar, ranging from 2.3 to 6.4 ‰. Chemical and isotope evidences

suggest that superimposed deformational events affecting some granites from the Papanduva Pluton played an important role in circulation of residual melts and fluid phases, at progressively more oxidizing conditions.

KEY-WORDS: ferromagnesian minerals, trace elements, oxygen isotope ratio, late- to post-magmatic evolution, peralkaline granites, Morro Redondo Complex, Graciosa Province

1. INTRODUCTION

Alkaline felsic rocks are marked by the ubiquity of clinopyroxenes and/or amphiboles as the main mafic phases. In particular, the precipitation of aegirine and arfvedsonite instead of fayalite or magnetite is a typical feature of the transition from metaluminous to peralkaline compositions (e.g. Markl et al., 2010; Marks et al., 2003). The petrogenetic importance of clinopyroxenes and amphiboles is justified by their significant chemical variability and the ability to incorporate a large amount of geochemically relevant trace elements (Wood and Blundy, 1997; Marks et al., 2003; 2004). Such characteristics turn these minerals into a powerful tool to unravel the chemical evolution of magmatic, late- to post-magmatic liquids and post-magmatic fluids from which they have crystallized (e.g. Aoki, 1964; Saviulo et al., 2000; Giret et al., 1980; Strong and Taylor, 1984; Marks et al., 2003; Marks et al. 2004a, 2004b; Gualda and Vlach, 2007; Schilling et al., 2011; Reguir et al., 2012).

Sodic-calcic and sodic clinopyroxenes and amphiboles are the main ferromagnesian minerals in peralkaline granites of the Papanduva Pluton, Morro Redondo Complex, in the Graciosa A-type Province, Southernmost Brazil. These granites are among the most evolved rocks within the province and also host a variety of rare HFSE-bearing accessory minerals. In common, amphiboles, clinopyroxenes and the rare accessory mineralogy crystallize during late- to post-magmatic stages, characteristics that turn the Papanduva Pluton into a particularly interesting site for mineralogical studies on oversaturated peralkaline rocks (e.g. Marks et al., 2011). In such a scenario, the accurate definition of compositional trends for the ferromagnesian minerals is crucial to better understand how peralkaline liquids and fluids evolved through the magmatic and post-magmatic

stages (e.g. Marks et al., 2003; Schilling et al., 2011). For instance, many works have shown that compositional variations registered in amphiboles can reflect the alumina saturation index and, consequently, the magma alkalinity degree, as well as the redox conditions during the crystallization (e.g. Carmichael et al., 1974; Giret et al., 1980; Strong and Taylor, 1984).

Hence, this work presents compositional variations and evolutionary trajectories registered in representative crystals of different amphiboles and clinopyroxenes generations from the Papanduva Pluton, combining textural studies, major and trace elements analyses (EPMA and LA-ICP-MS) and O stable isotope data. We also offer important inferences on crystallization conditions and late- to post-magmatic evolution, including substitution reactions between these minerals, redox conditions, as well as on the role of deformational events in controlling the liquid composition and circulation.

2. GEOLOGICAL BACKGROUND

A-type granites of peralkaline affinity constitute the Papanduva Pluton of ca. 60 Km² in the northern part of the Morro Redondo Complex. The complex also includes a distinct pluton (Quiriri) made of aluminous “subalkaline” A-type biotite-bearing granites and associated bimodal volcanic rocks, covering a total area of about 250 Km². The complex is part of the post-collisional Graciosa Province of A-type granites and syenites (Gualda and Vlach, 2007a) formed during extensional tectonic regimes related to Gondwana amalgamation, at the final stages of the Brasiliano/Pan-African Orogeny in S-SE Brazil, at 580 – 586 Ma (Vlach et al., 2010; Vilalva et al, submitted). Further details of the Graciosa Province can be found in the works by Gualda and Vlach (2007a, 2007b), Vlach and Gualda (2007) and Vlach et al. (2010).

The Papanduva Pluton, and the Morro Redondo Complex as a whole, is described in detail by Vilalva (2007) and Vilalva and Vlach (submitted). We here depict its main petrographic and geochemical features. The rocks are essentially leucocratic ($M' = 2 - 9$) alkali-feldspar granites with variable quartz contents grouped into four main petrographic facies, as follows:

- 1) *Massive facies*: slightly inequigranular, coarse- to medium-grained massive granites with both sodic-calcic and sodic amphiboles and clinopyroxenes. It corresponds to the main facies and crops out in the central and SW pluton areas.

2) *Protomylonitic facies*: porphyroclastic, protomylonitic or mylonitic granites related with late- to post-magmatic deformational events. Textures are characterized by porphyroclasts of sodic amphibole, alkali-feldspar and quartz in a saccharoidal fine-grained quartz-feldspathic matrix with sodic clinopyroxene. Further, the matrix often displays an “agpaitic” accessory mineralogy, including narsarsukite, aenigmatite, neptunite, britholite, elpidite and other (Zr-Na)-bearing silicates and turkestanite. The facies is restricted to the outer pluton areas, mainly around the massive facies.

3) *Cataclastic facies*: slightly deformed coarse- to medium-grained granites with sodic clinopyroxene in aggregates of many crystals as the main mafic mineral. It is restricted to a small area at the northernmost pluton area.

4) *Microgranitic facies*: slightly inequigranular fine-grained granites forming dykes intrusive into rocks from the massive facies, as well the granites from the Quiriri Pluton. Planar flow structures defined by euhedral sodic amphibole or clinopyroxene are observed.

In common, all rock varieties are characterized by high alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 8.7$ to 9.3 wt. %) and iron [Fe# number = $\text{FeO}/(\text{FeO} + \text{MgO})$ mol. ≥ 0.96] contents, with Agpaitic Index [AI = $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ mol.] and Alumina Saturation Index [ASI = $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ mol.] values between $1.04 - 1.28$ and $0.76 - 0.94$, respectively, common features of evolved peralkaline A-type granites (e.g. Frost et al., 2001; Frost and Frost, 2011). High-field strength elements (HFSE) contents are also relatively high, especially Zr, Nb, Y and the rare-earth elements (REE), with abundances up to 2430, 88, 320 and 996 ppm, respectively. Magnetic susceptibilities are typically low ($< 10^{-3}$ SI) due to the lack of Fe-Ti oxides, mainly magnetite in most of the petrographic facies. Nevertheless, some high values, up to 6.0×10^{-3} SI, are registered in few samples from the cataclastic facies containing post-magmatic magnetite (see section 4).

3. ANALYTICAL METHODS AND DATA TREATMENT

A combined In-situ chemical and stable isotope compositional study were conducted in selected amphiboles and clinopyroxenes crystals of different textural generations in representative samples of the four petrographic facies of the Papanduva Pluton, preferentially along core – rim profiles. Major- and minor-elements compositions were obtained in $30\ \mu\text{m}$ thick polished-thin rock sections

by electron-probe microanalyses (EPMA) conducted at the Electron Microprobe Facility of the Geosciences Institute, University of São Paulo (IGc-USP), Brazil, while trace-elements were quantified in 60 – 80 µm thick polished-thin sections by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses realized at the MITERAC Facility, University of Notre Dame, USA and at the Laboratory of Chemistry and ICP-OES/MS of the Geosciences Institute, University of São Paulo. Stable oxygen isotope ratios were measured in hand-picked mineral grains at the CEST facility, University of Notre Dame.

3.1. EPMA ANALYSIS

Quantitative WDS microanalyses were obtained using a Jeol JXA-8600S equipped with 5 WD and 1 ED spectrometers, each one of them with two analyzer crystals (STE/TAP, TAP/PET, PET/LiF, PET/LiF, PET/LiF), automated by the Thermo-Noran Voyager 4.3.1 system. Analytical conditions were 15 kV for the column acceleration, 20 nA and 5 µm for beam current and diameter at the sample surface, respectively and maximum pulse integration times between 10 to 40 s. Quantified spectral lines, employed analyzer crystals and standards were: $\text{SiK}\alpha$ (TAP, wollastonite), $\text{TiK}\alpha$ (LiF, rutile), $\text{ZrK}\alpha$ (PET, zircon), $\text{AlK}\alpha$ (TAP, honblende), $\text{FeK}\alpha$ and $\text{MnK}\alpha$ (LiF, Mn-olivine), $\text{MgK}\alpha$ (TAP, diopside), $\text{ZnK}\alpha$ (LiF, ZnO synth), $\text{CaK}\alpha$ (PET, wollastonite), $\text{NaK}\alpha$ (TAP, albite), $\text{KK}\alpha$ (PET, microcline). Further, $\text{ClK}\alpha$ (PET, apatite) and $\text{FK}\alpha$ (TAP, apatite) were also measured for amphiboles.

For structural formulae calculations, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ partition for the clinopyroxenes were computed considering 4 total cations and 6 O, after Droop (1987). For the amphiboles, iron partition followed the procedures described in Gualda and Vlach (2005). Furthermore, average Li_2O contents derived from the LA-ICP-MS were considered in amphiboles structural formulae calculations, following Hawthorne et al. (1993) who showed that Li can be an important component in sodic amphiboles and, by omitting its presence, overestimated Si contents in the tetrahedral site [T] and consequent deficiency in the octahedral site [C] are detected.

3.1.1. *Pyroxene end-members calculation scheme*

The calculation of end-members for pyroxene-group minerals is an important complement in classification proposals since it allows, in many cases, to establish evolutionary trends, as well as to characterize subtle compositional changes that are hardly identified in cationic diagrams (e.g. Ulbrich, 1986). A large number of pyroxene end-members can be found in the literature, but the IMA recommended nomenclature scheme described by Morimoto (1988) only uses 13 molecules to represent the extreme end-members. We followed the procedures after Morimoto (1988) to classify the clinopyroxenes according to the IMA recommendations. In many cases, however, such a simplification leads to misguided classifications due to: 1) not considering intermediate compositions in a solid-solution that are typical of certain rocks; or 2) it does not accommodate many elements that can appear in relatively high abundances in certain pyroxenes and define theoretical end-members that, although not formally recognized by IMA, are still largely used to describe specific evolutionary trends and crystallization conditions (e.g. Cawthorn and Collerson, 1974; Grapes et al., 1979). In particular, sodic pyroxenes can contain significant amounts of Ti and Zr (as discussed later on this work), elements that are not incorporated into any of the molecules considered by Morimoto (1986) (i.e. $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ – aegirine and $\text{NaAlSi}_2\text{O}_6$ – jadeite). For instance, Nielsen (1979) presents aegirine analyses showing TiO_2 contents up to 6.0 – 8.0 wt. %, while Njonfang and Nono (2003) describe aegirine with TiO_2 and ZrO_2 abundances between 4.0 – 6.0 wt. % and 2.0 – 4.0 wt. %, respectively (see also Ferguson, 1977; Dyulgerov and Platevoet, 2006). In this work, we have analyzed some truly titanian aegirine crystals with TiO_2 up to 7.0 wt. % and ZrO_2 up to 1.4 wt. %. Following the method after Morimoto (1988), overestimated quantities of aegirine (Fe^{3+}) and ferrosilite (Fe^{2+}) end-members and low totals are registered. Hence, to better discuss evolutionary trends and compositional variations intra- and inter-crystals, we also adopted in parallel the calculation method after Grapes et al. (1979) that allows Ti and Zr to form the theoretical end-members FM-NAT: $\text{NaTi}_{0.5}(\text{FM})_{0.5}\text{Si}_2\text{O}_6$ (where $\text{FM} = \text{Fe}^{2+} + \text{Mn} + \text{Zn} + \text{Mg}$; e.g. Ferguson, 1977) and FM-NAZ: $\text{NaZr}_{0.5}(\text{FM})_{0.5}\text{Si}_2\text{O}_6$ (Jones and Peckett, 1980), respectively. In our calculations, the NAT and NAZ molecules were derived from the generic molecule $\text{Na}(\text{Ti}, \text{Zr})_{0.5}(\text{FM})_{0.5}\text{Si}_2\text{O}_6$.

3.2. LA-ICP-MS ANALYSES

Trace element abundances were quantified using a Elan 6100DRC (University of São Paulo) and a ThermoFinnigan Element2 (University of Notre Dame) ICP-MS instruments, both coupled to a ESI-New Wave Research UP-213 laser ablation system. Amphiboles and clinopyroxenes crystals were ablated using a laser spot of 40 μm under a repetition rate of 4 Hz and energy fluence of $\sim 15 \text{ J/cm}^2$. The following ion masses were scanned: Li^7 , Be^9 , P^{31} , Ca^{43} , Sc^{45} , Ti^{49} , V^{51} , Cr^{52} , Mn^{55} , Co^{59} , Ni^{60} , Cu^{65} , Zn^{66} , Ga^{71} , Rb^{85} , Sr^{88} , Y^{89} , Zr^{90} , Nb^{93} , Mo^{95} , Sn^{118} , Sb^{121} , Cs^{133} , Ba^{137} , La^{139} , Ce^{140} , Pr^{141} , Nd^{143} , Sm^{147} , Eu^{151} , Gd^{155} , Tb^{159} , Dy^{163} , Ho^{165} , Er^{166} , Tm^{169} , Yb^{173} , Lu^{175} , Hf^{179} , Ta^{181} , Pb^{208} , Th^{232} and U^{238} , during a total acquisition time of 120 s, equally divided between background and laser ablation ion signal measurements using a rapid peak jumping (dwell time for each mass = 8.0 ms), and followed by 30 s of washout time. Synthetic glasses NIST SRM 612 and BHVO-2G (only at the University of São Paulo's ICP-MS facility) were used as external standard, while average ^{43}Ca contents obtained from the EPMA analyses were employed as internal standard. Drift correction, data reduction and elemental abundance determinations were achieved using the Glitter software (van Achterbergh et al., 2001).

3.3. OXYGEN STABLE ISOTOPE ANALYSES

In-situ stable O isotope ratios of amphiboles and clinopyroxenes, as well as coexisting quartz were obtained using a ESI-New Wave Research MIR-10 laser fluorination system coupled to a silicate extraction line (method after Sharp, 1990), and measured using a Thermo Fisher Scientific Delta V Plus mass spectrometer. Individual mineral separates, weighing ~ 0.6 to 3.0 milligrams – obtained after careful manual sample crushing and milling and picking under a stereoscope –, were placed into separate tapered holes within a nickel block, which is later housed within a stainless steel sample chamber that contains a BaF_2 window. Upon heating with a CO_2 -based (infrared) laser, the sample undergoes reaction and liberates O_2 gas along with other gases (e.g. SiF_4 for quartz). The extraction line consists of inert stainless steel tubing that contains various cold and heated traps for purification of the oxygen gas. The O_2 gas is then trapped into a sealed and frozen quartz vial and upon subsequent heating is flushed to the mass spectrometer with a stream of He

gas. The ($O_2 + He$) gas mixture enters a gas chromatographic column that is connected directly to the inlet of the mass spectrometer. Instrumental fractionation of the $^{18}O/^{16}O$ isotope ratios was monitored via repeated analysis of the synthetic Lausanne Quartz standard (certified $^{18}O/^{16}O$ value = 18.15 ‰; Jourdan et al., 2009) using a “sample-standard” bracketing technique during each analytical session.

4. TEXTURAL FEATURES

4.1. CLINOPYROXENES

Clinopyroxenes are ubiquitous phases in all petrographic facies of the Papanduva Pluton, being the main mafic mineral in the cataclastic facies and some varieties within the microgranitic facies. Four distinct textural generations are recognized: (1) Cpx I – late-magmatic greenish to yellowish clinopyroxene; (2) Cpx II – post-magmatic greenish to yellowish clinopyroxene, typically as mantles over amphiboles; (3) Cpx III – late- to post-magmatic orange-yellowish clinopyroxene; and (4) Cpx IV – post-magmatic dark-green clinopyroxene.

Cpx I is the most common type in all petrographic facies. It is characterized by a discrete greenish pleochroism pattern, where X = green to yellow-green, Y = pale yellow-green (rosy), Z = green to pale-yellow. Compositional zoning are sectorial and concentric, with dark colored cores and light rims (Figs 1A, 1B). They appear as subhedral to euhedral individual crystals, as well as interstitial phases between quartz and alkali feldspar or forming fibrous aggregates, mainly in the cataclastic facies. Complex textural relationships between Cpx I and aenigmatite (Fig. 1B) and narsarsukite, including resorption and mantling are evidences of late- to post-magmatic and/or hydrothermal substitution reactions. Furthermore, microinclusions of fluorite are relatively common, especially in the protomylonitic facies.

Cpx II defines a distinct post-magmatic generation, yet displaying a pleochroism similar to the Cpx I pattern. It substitutes sodic and sodic-calcic amphiboles along fracture and cleavage planes or mainly around crystal rims, forming continuous or discontinuous mantles. Laths of albite, as well as quartz and fluorite are common inclusions.

Cpx III is a rare variety and it was only identified in a few samples of the protomylonitic, cataclastic and massive facies. The characteristic pleochroism is defined by X = pale-green; Y = pale orange to green; and Z = pale greenish-orange. Crystal cores are preferentially orange, while rims are greenish, defining a discrete concentric compositional zoning. Textural evidences suggest crystallization during late- to post-magmatic stages, after Cpx I precipitation (Fig. 1E).

Lastly, the Cpx IV are interpreted as a post-magmatic phase showing a typical dark-green pleochroism where X = yellowish dark-green, Y = dark-green and Z = olive-green. The Cpx IV is also a somewhat rare phase and can be found in some samples from the protomylonitic and massive facies as homogeneous crystals showing no compositional zoning, generally as interstitial phases between quartz and alkali-feldspar, sometimes in poikilitic-like textures with quartz and laths of post-magmatic albite (Fig. 1F).

The clinopyroxenes crystallization sequences and their positioning related to the amphiboles during the magmatic and post-magmatic stages are presented in Figure 2.

4.2. AMPHIBOLES

Amphiboles, including sodic and sodic-calcic varieties, are the most common mafic minerals in the Papanduva Pluton. As depicted in Figure 2, the amphiboles are mainly magmatic phases, except for the cataclastic and microgranitic facies where some post-magmatic generations are also identified.

Figure 1: (A) Crystal of type-I clinopyroxene (Cpx I) zoning well-marked compositional zoning, close to sodic amphibole (Na-Amp) in matrix made of quartz (Qtz) and potassic feldspar (Kfs) of protomylonitic alkali feldspar granite. (B) Crystal of type-I clinopyroxene (Cpx I) containing anhedronal relicts of aenigmatite (Eng) interstitial to quartz (Qtz) and potassic feldspar (Kfs) in protomylonitic alkali feldspar granite. The green-colored core where aenigmatite relicts are found are Ca-, Ti- and Fe^{2+} -rich. (C) Post-magmatic type-II clinopyroxene (Cpx II) crystals appearing as mantles over sodic amphibole porphyroclast (Na-Amp) in a quartzose (Qtz) matrix of protomylonitic alkali feldspar. Quartz also appears as inclusions in the amphibole. (D) Type II clinopyroxene (Cpx II) crystals with irregular compositional zoning patterns mantling sodic-calcic amphibole (Na-Ca-Amp) from massive alkali feldspar granite. (E) Type-III clinopyroxene crystal showing typical orange colors among sodic amphibole (Na-Amp), type-I and -IV clinopyroxenes (Cpx-I and Cpx-IV), quartz (Qtz) and potassic feldspar (Kfs) in protomylonitic alkali feldspar granite. (F) Interstitial type-IV clinopyroxene (Cpx-IV) showing poikilitic-like texture encompassing albite laths and anhedronal crystals (Ab) between alkali feldspar crystals (Afs) in massive alkali feldspar granite. All photomicrographs obtained under plane polarized light.

mineral phase	crystallization stage		
	magmatic	late magmatic	post-magmatic
(Na-Ca)-Amphiboles	...		
(Na)-Amphiboles		arfvedsonite	riebeckite ...
Cpx I		...	
Cpx II			...?
Cpx III		? ..	?
Cpx IV			..

Figure 2: Crystallization sequence chart for clinopyroxenes and amphiboles from the Papanduva Pluton.

Sodic amphiboles are predominant and crystallize as isolated or aggregates of 3 – 5 subhedral to anhedral crystals (1.0 to 5.0 mm long) with brownish-green to dark blue pleochroism colors, filling in interstices between quartz and alkali feldspar (Figs 3A-C). Irregular sectorial and concentric compositional zoning, alternating dark cores and light rims (Fig. 1A), are better registered in the protomylonitic facies where amphiboles appear as fractured, elongate or rounded porphyroclasts (Figs. 1C, 3B). Conversely, sodic-calcic amphiboles define an earlier generation restricted to the granites of massive facies. They appear as aggregates of 2 – 3 subhedral crystals (2.0 – 6.0 mm long) displaying bluish-green pleochroism colors (Figs 1D, 3E, 3F). Compositional zoning are discrete or absent.

Late- to post-magmatic and hydrothermal substitution reactions lead to the crystallization of a variety of minerals along amphiboles rims and fracture/cleavage planes. Aegirine mantles (Figs. 1C, 1D, 3B, 3D, 3E) and fibrous astrophyllite are the most frequent. The former can be found in samples from all petrographic facies, while the latter are lacking in the microgranitic facies. Moreover, magnetite crystals are typical in amphiboles from the cataclastic (Fig. 3C) and microgranitic facies, while neptunite (Fig. 3B) and narsarsukite are typical from the protomylonitic facies.

Figure 3: (A) Sodic amphibole crystals (Na-Amp) with well-marked compositional zoning filling in spaces among quartz (Qtz), post-magmatic albite (Ab) and type-I clinopyroxene (Cpx I) in protomylonitic alkali feldspar granite. (B) Sodic amphibole porphyroclast (Na-Amp) among quartz crystals (Qtz) in protomylonitic alkali feldspar granite. Neptunite (Npt) and type-II clinopyroxene (Cpx II) replace the amphibole along fracture planes and rims. Quartz inclusions are concentrated in the core region. (C) Sodic amphibole crystal (Na-Amp) showing post-magmatic magnetite crystals (Mag) along the cleavage and fracture planes, as well as close to the rim zones. The amphibole is also mantled by type-II clinopyroxene (Cpx II) and appears among quartz crystals (Qtz) in cataclastic alkali feldspar granite. (D) Sodic amphibole crystals (Na-Amp) partially replaced by type-II clinopyroxene (Cpx II) filling in spaces between quartz (Qtz) and alkali feldspar (Afs) crystals of cataclastic alkali feldspar granite. An euhedral zircon crystal (Zrn) also appears close to the amphibole. (E) Sodic-calcic amphibole crystals (Na-Ca-Amph) with quartz (Qtz) and zircon (Zrn) inclusions, interstitial to

Figure 3 (cont.): quartz (Qtz) and alkali feldspar (Afs) crystals in massive alkali feldspar granite. (F) Detail of a sodic amphibole overgrowth (white arrows) over sodic-calcic amphibole crystal (Na-Ca-Amph) showing quartz (colorless) and zircon (Zrn) inclusions in massive alkali feldspar granite.

5. MINERAL CHEMISTRY: MAJOR AND MINOR COMPOSITIONS (EPMA)

A total of ca. 500 individual WDS analyses in amphiboles and clinopyroxenes from all petrographic facies of the Papanduva Pluton were performed. Representative analyses and structural formulae of the main textural generations of clinopyroxenes and amphiboles from the Papanduva Pluton are listed in Tables I and II and discussed below.

5.1. CLINOPYROXENES

Yellow-greenish clinopyroxenes (Cpx I and II) correspond to an aegirine, with compositions defined within the interval $\text{Eg}_{81-99}\text{Jd}_{0-5}\text{WEF}_{0-15}$. Orange-yellowish clinopyroxene (Cpx III) is an almost pure aegirine ($\text{Eg}_{93-97}\text{Jd}_{1-3}\text{WEF}_{2-5}$), while dark-green clinopyroxene (Cpx IV) classifies as aegirine-augite with compositions ranging within the interval $\text{Eg}_{72-80}\text{Jd}_1\text{WEF}_{18-27}$.

Aegirines I and II were grouped together for discussions in this section, since no substantial differences are observed between major and minor compositions of these clinopyroxenes. However, it is worth to mention that crystals of aegirine II replacing sodic-calcic amphiboles in the massive facies show compositions that are more calcic (up to 1.97 wt. % CaO) than those crystals replacing sodic amphiboles in the other facies (ca. 0.5 wt. % CaO). Compositions are characterized by relatively high Ti (up to 6.9 wt. % TiO_2) and Zr (up to 1.11 wt. % ZrO_2) contents (Table I). Ca reaches its maximum abundances in crystals from the protomylonitic (up to 4.0 wt. % CaO) and massive facies (up to 2.0 wt. % CaO), and Al is slightly higher in the microgranitic facies (0.23 – 0.96 wt. % Al_2O_3). Conversely, the aegirine III shows higher, yet variable, Mn (up to 0.97 wt. % MnO) and Zn (up to 0.44 wt. % ZnO) contents and the aegirine-augite (Cpx IV) registers relatively lower Ti (up to 3.2 wt. % TiO_2) and higher Zr (up to 1.3 wt. % ZrO_2) abundances when compared to aegirines I and II.

Table I: representative WDS compositions (wt. %) and structural formulae for clinopyroxene from the Papanduva Pluton. Point_ID: spot identification. K₂O gave concentrations below the detection limit in all analyses and was omitted. b.d.l.: below detection limit.

Clinopyroxene	Cpx I								Cpx II				Cpx III		Cpx IV			
Sample	MR-41		MR-01A		MR-61		MR-68		MR-49 (1)		MR-107		MR-06		MR-06		MR-121	
Crystal	c2-1	c2-1	c.1-1 z	c.1-1 z	c5-1	c5-1	x3-xtal2	x3-xtal2	c4-1	c4-1	c2-1	c2-1	c1-2	c1-2	c1-1 v esc	c1-1 v esc	c7-1	c7-1
Point_ID	7, rim	9, core	2, core	4, rim	1, rim	2, core	1, n	2, b	1, rim	2, core	5, core	8, core	2, n	3, b	2, b	3, n	3, n	1, b
Facies	protomylonitic		cataclastic		massive		microgranitic		protomylonitic		massive		protomylonitic		protomylonitic		massive	
SiO ₂	52.51	52.25	51.86	51.62	51.99	51.72	52.30	52.51	51.72	52.30	50.79	51.95	52.13	52.05	50.71	50.46	51.06	51.07
TiO ₂	1.04	6.24	0.71	2.15	1.39	2.09	1.33	1.35	1.25	2.13	2.08	1.97	1.31	1.28	0.54	0.46	1.81	2.12
Al ₂ O ₃	0.15	0.20	0.25	0.20	0.33	0.32	0.59	0.60	0.30	0.19	0.23	0.33	0.26	0.38	0.26	0.23	0.25	0.23
ZrO ₂	b.d.l.	0.06	0.60	1.11	0.03	0.18	0.08	0.08	0.05	0.12	0.14	0.05	0.05	0.10	b.d.l.	b.d.l.	1.05	1.27
Fe ₂ O ₃	30.89	20.44	29.26	26.14	31.11	26.39	28.79	29.78	31.79	27.92	25.18	27.67	30.29	30.23	24.33	26.64	22.37	20.63
FeO	2.51	6.70	2.82	4.45	1.47	5.01	1.64	2.08	0.76	4.26	5.87	3.55	1.45	0.74	8.42	5.84	7.32	8.94
MnO	0.07	0.31	0.17	0.28	0.08	0.15	0.45	0.37	0.24	0.15	0.20	0.12	0.96	0.97	0.34	0.24	0.26	0.29
MgO	b.d.l.	b.d.l.	0.03	b.d.l.	0.11	0.11	0.13	0.12	b.d.l.	b.d.l.	0.03	0.03	0.04	0.06	0.03	b.d.l.	0.16	0.13
ZnO	0.07	0.08	0.03	b.d.l.	0.01	0.03	0.14	0.13	0.05	0.11	b.d.l.	b.d.l.	0.35	0.44	0.03	0.06	0.09	0.13
CaO	0.37	0.40	0.40	1.33	0.13	1.97	0.44	0.43	0.16	0.47	3.60	0.50	0.28	0.34	5.49	4.89	3.82	4.80
Na ₂ O	13.07	13.05	12.82	12.47	13.27	12.05	13.10	13.09	13.29	12.81	11.20	12.85	13.02	13.11	9.74	10.42	10.88	10.35
Sum	100.67	99.73	98.94	99.78	99.90	100.04	98.98	100.54	99.65	100.47	99.33	98.99	100.14	99.69	99.93	99.26	99.08	99.96
<i>Structural formulae based on 4 cations and 6 O, according to Droop et al. (1987)</i>																		
Si	2.007	2.005	2.017	1.999	1.996	1.997	2.019	2.003	1.992	2.005	1.985	2.014	2.002	2.004	1.990	1.984	2.004	1.997
Al	0.000	0.000	0.000	0.001	0.004	0.003	0.000	0.000	0.008	0.000	0.011	0.000	0.000	0.000	0.010	0.011	0.000	0.003
Fe3+	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.005	0.000	0.000
Sum T	2.007	2.005	2.017	2.000	2.000	2.000	2.019	2.003	2.000	2.005	2.000	2.014	2.002	2.004	2.000	2.000	2.004	2.000
Al	0.007	0.009	0.011	0.008	0.011	0.011	0.027	0.027	0.006	0.009	0.000	0.015	0.012	0.017	0.002	0.000	0.012	0.008
Fe3+	0.888	0.590	0.856	0.762	0.899	0.767	0.836	0.855	0.921	0.806	0.737	0.807	0.876	0.876	0.718	0.784	0.661	0.607
Ti	0.030	0.180	0.021	0.063	0.040	0.061	0.039	0.039	0.036	0.061	0.061	0.057	0.038	0.037	0.016	0.014	0.054	0.062
Zr	0.000	0.001	0.011	0.021	0.001	0.003	0.001	0.002	0.001	0.002	0.003	0.001	0.001	0.002	0.000	0.000	0.020	0.024
Zn	0.002	0.002	0.001	0.000	0.000	0.001	0.004	0.004	0.001	0.003	0.001	0.000	0.010	0.012	0.001	0.002	0.002	0.004
Mg	0.001	0.000	0.001	0.001	0.006	0.006	0.007	0.007	0.001	0.000	0.002	0.002	0.002	0.003	0.002	0.001	0.009	0.007
Fe2+	0.072	0.215	0.092	0.144	0.043	0.151	0.053	0.067	0.025	0.119	0.192	0.115	0.047	0.024	0.261	0.192	0.240	0.287
Mn	0.000	0.002	0.006	0.001	0.000	0.000	0.015	0.001	0.008	0.000	0.006	0.003	0.015	0.029	0.000	0.008	0.002	0.000
Sum M1	1.000	1.000	1.000	1.000	1.000	1.000	0.982	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Fe2+	0.008	0.000	0.000	0.000	0.004	0.011	0.000	0.000	0.000	0.018	0.000	0.000	0.000	0.000	0.015	0.000	0.000	0.005
Mn	0.002	0.008	0.000	0.008	0.003	0.005	0.000	0.011	0.000	0.005	0.001	0.001	0.016	0.003	0.011	0.000	0.007	0.010
Ca	0.015	0.017	0.017	0.055	0.005	0.082	0.018	0.017	0.007	0.019	0.151	0.021	0.012	0.014	0.231	0.206	0.160	0.201
Na	0.968	0.971	0.966	0.937	0.988	0.902	0.981	0.968	0.993	0.952	0.849	0.965	0.970	0.979	0.741	0.795	0.828	0.785
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000
Sum M2	0.993	0.996	0.983	1.000	1.000	1.000	0.999	0.997	1.000	0.995	1.000	0.987	0.998	0.996	0.999	1.000	0.996	1.001
<i>Classification end-members after Morimoto (1988)</i>																		
Q	0.1	0.2	0.1	0.0	0.1	0.2	0.4	0.3	0.0	0.2	0.1	0.1	0.1	0.0	11.6	10.4	0.4	0.5
J	1.9	1.9	4.5	7.0	2.0	1.8	2.6	3.3	2.0	1.9	9.4	5.6	1.9	2.0	9.4	0.0	1.7	1.6
WEF	4.7	10.7	5.4	9.7	2.9	12.2	3.9	4.5	1.2	6.6	16.9	6.6	3.0	2.1	13.9	9.7	19.9	24.2
EG	94.6	88.0	93.4	89.3	95.5	86.2	93.2	92.6	97.0	91.4	82.0	91.7	95.7	96.1	25.5	20.1	78.7	74.5
JD	0.7	1.3	1.2	1.1	1.6	1.6	3.0	2.9	1.4	1.0	1.2	1.7	1.3	1.9	73.2	78.9	1.4	1.3

Table II: representative WDS compositions (wt. %) and structural formulae for amphiboles from the Papanduva Pluton. Structural formulae computed according to Schumacher (1997) and Gualda and Vlach (2005). Point_ID: spot identification. b.d.l: below detection limit

Amphibole	ferrichterite				arfvedsonite								riebeckite			
	MR-39		MR-121		MR-02A		MR-107		MR-61		MR-90A		MR-11 (A)		MR-01 D	
	c3-1		c4-1		c2-1		c5-1		c4-1		c1-1		c1-1		c3-1	
	1, rim	2, core	1, rim	3, core	4, core	6, rim	1, rim	3, core	1, rim	3, core	4, rim	2, core	1, rim	2, core	1, rim	3, core
Facies	massive				protomylonitic				massive		microgranitic		cataclastic		microgranitic	
SiO ₂	48.78	47.46	48.3	48.2	50.9	50.0	49.3	49.4	50.2	49.9	49.8	49.3	50.2	50.2	50.1	50.1
TiO ₂	1.65	1.59	1.66	1.52	1.28	0.15	0.87	2.51	1.70	1.70	0.74	0.69	0.91	0.40	1.11	1.07
ZrO ₂	0.11	0.08	0.03	b.d.l.	0.10	0.02	b.d.l.	b.d.l.	0.07	b.d.l.	0.06	b.d.l.	0.03	0.44	b.d.l.	0.08
Al ₂ O ₃	1.04	1.91	1.61	1.62	0.62	0.14	0.06	0.15	0.40	0.73	0.64	0.64	0.49	1.08	0.62	0.82
Li ₂ O*	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Fe ₂ O ₃	5.07	3.16	4.51	5.24	2.79	8.27	6.64	2.37	7.46	6.02	10.7	9.45	12.3	13.5	11.2	11.7
FeO	28.8	29.7	29.8	28.5	31.0	27.6	27.6	30.5	26.1	27.3	25.1	25.8	23.7	24.7	24.7	24.6
MnO	0.70	0.74	0.76	0.74	0.55	0.65	0.73	0.81	0.62	0.66	0.60	0.60	0.57	0.63	0.76	0.59
ZnO	0.16	0.21	0.17	0.28	0.20	0.33	0.27	0.25	0.36	0.18	0.34	0.32	0.28	0.19	0.37	0.29
MgO	0.60	0.69	0.73	0.67	0.07	0.07	0.08	0.02	0.48	0.43	0.02	0.02	0.33	0.11	0.06	0.06
CaO	3.08	4.45	3.08	3.25	1.09	0.13	0.44	0.89	0.81	2.03	0.70	0.98	0.33	1.06	1.10	1.42
Na ₂ O	5.91	5.46	6.21	6.09	8.73	7.44	7.28	8.03	7.17	6.48	7.40	7.54	6.64	6.34	6.20	6.01
K ₂ O	1.46	1.43	1.60	1.57	1.65	3.88	3.37	2.13	2.02	1.84	1.47	1.27	1.81	0.14	1.67	1.63
F	0.34	0.50	0.13	0.27	0.86	0.53	0.42	0.37	0.50	0.82	0.80	1.14	0.37	0.10	0.62	0.72
Cl	b.d.l.	0.03	0.03	0.03	0.02	b.d.l.	b.d.l.	b.d.l.	0.02	0.02	0.02	0.02	b.d.l.	b.d.l.	b.d.l.	0.03
Sum1	97.7	97.5	98.7	98.1	100.1	99.5	97.3	97.7	98.1	98.4	98.6	98.0	98.3	99.2	98.8	99.4
O=F=Cl	0.14	0.22	0.06	0.12	0.37	0.23	0.18	0.16	0.21	0.35	0.34	0.48	0.16	0.04	0.26	0.31
Sum	97.6	97.3	98.6	98.0	99.8	99.3	97.1	97.5	97.9	98.1	98.3	97.5	98.1	99.2	98.5	99.1
Si	7.819	7.679	7.698	7.711	8.019	7.974	8.001	7.972	7.953	7.926	7.891	7.904	7.909	7.802	7.885	7.850
Al	0.181	0.321	0.302	0.289	0.000	0.026	0.000	0.028	0.047	0.074	0.109	0.096	0.091	0.198	0.115	0.150
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum T	8.000	8.000	8.000	8.000	8.019	8.000	8.001	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al	0.015	0.044	0.000	0.017	0.116	0.000	0.011	0.000	0.028	0.062	0.010	0.024	0.000	0.000	0.000	0.000
Ti	0.199	0.193	0.199	0.183	0.152	0.018	0.106	0.304	0.202	0.203	0.088	0.083	0.108	0.047	0.131	0.126
Fe ³⁺	0.611	0.384	0.540	0.632	0.330	0.992	0.811	0.288	0.890	0.720	1.278	1.140	1.457	1.581	1.331	1.377
Zr	0.008	0.006	0.002	0.001	0.008	0.001	0.000	0.000	0.006	0.000	0.004	0.000	0.003	0.033	0.000	0.006
Zn	0.018	0.025	0.020	0.033	0.023	0.039	0.032	0.029	0.042	0.021	0.040	0.038	0.033	0.022	0.043	0.033
Mg	0.143	0.166	0.174	0.161	0.016	0.017	0.019	0.004	0.114	0.101	0.004	0.005	0.077	0.026	0.015	0.015
Li	0.055	0.056	0.000	0.055	0.171	0.157	0.176	0.150	0.172	0.172	0.172	0.174	0.129	0.001	0.124	0.144
Fe ²⁺	3.855	4.024	3.968	3.819	4.092	3.687	3.743	4.114	3.463	3.632	3.323	3.455	3.118	3.207	3.254	3.220
Mn	0.094	0.102	0.097	0.100	0.074	0.088	0.100	0.111	0.083	0.089	0.080	0.081	0.076	0.083	0.102	0.078
Sum C	5.000	5.000	5.000	5.000	4.981	5.000	4.999	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Li	0.000	0.000	0.055	0.000	0.000	0.016	0.000	0.025	0.000	0.000	0.000	0.000	0.042	0.167	0.047	0.026
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.529	0.771	0.526	0.558	0.184	0.023	0.077	0.154	0.137	0.346	0.119	0.169	0.055	0.176	0.186	0.237
Na	1.471	1.229	1.413	1.442	1.816	1.961	1.923	1.821	1.863	1.654	1.881	1.831	1.902	1.656	1.768	1.736
Sum B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.367	0.484	0.505	0.449	0.851	0.339	0.367	0.690	0.342	0.340	0.392	0.511	0.125	0.254	0.126	0.089
K	0.299	0.295	0.324	0.321	0.332	0.789	0.697	0.438	0.408	0.373	0.298	0.260	0.363	0.028	0.335	0.326
Sum A	0.666	0.779	0.829	0.770	1.183	1.128	1.064	1.128	0.750	0.713	0.689	0.771	0.487	0.281	0.461	0.415
F	0.170	0.254	0.067	0.135	0.429	0.269	0.216	0.190	0.249	0.413	0.403	0.577	0.184	0.047	0.310	0.358
Cl	0.003	0.009	0.009	0.007	0.005	0.003	0.001	0.000	0.004	0.006	0.005	0.005	0.001	0.002	0.002	0.007
Cations	15.839	16.042	15.904	15.912	16.617	16.401	16.280	16.318	16.003	16.133	16.097	16.353	15.672	15.329	15.772	15.780

5.1.1. *Intracrystal compositional variations*

Intracrystal compositional variations and zoning patterns are strongly defined for aegirines I and II and discrete in aegirine III. Similar variations, yet restricted and subtle, are registered for the aegirine-augite.

Figure 4 shows a rim-core-rim zoning profile (A-B) for an aegirine I crystal displaying irregular concentric and sectorial zoning patterns that describes quite well the main compositional variations registered in the clinopyroxenes from the Papanduva Pluton. The zoning pattern is defined by a dark irregular shaped core surrounded by light green and yellow intermediate and rim zones (Fig. 4 – i). BSE images confirm the irregular concentric pattern, with low BSE intensities in the core contrasting with high intensities in the intermediated and rim zones (Fig. 4 – ii). The zoning profile A-B registers increasing Fe^{3+} (0.561 to 0.854 a.p.f.u.) and Na (0.950 to 0.968 a.p.f.u.) abundances parallel to decreasing Ti (0.185 to 0.012 a.p.f.u.), Ca (0.038 to 0.004 a.p.f.u.), Fe^{2+} (0.238 to 0.034 a.p.f.u.) and Mn (0.013 a 0.001 a.p.f.u.) from core to crystal rims. Al shows an irregular behavior, but, in overall, its contents decrease from core to intermediate zones and crystal rims (0.006 a 0.003 a.p.f.u.). Conversely, the outermost crystal zones record an increasing of Ti (0.110 a.p.f.u.), Al (0.02 a.p.f.u.), Fe^{2+} (0.094 a.p.f.u.) and Na (0.995 a.p.f.u.) contents and depletion of Fe^{3+} (0.790 a.p.f.u.) (Fig. 4). It is interesting to point out that some aegirine I crystals from the cataclastic facies reveal an opposite pattern, with increasing Ca and decreasing Na towards crystal rims.

5.2. AMPHIBOLES

The amphiboles from the Papanduva Pluton span a relatively narrow compositional range, including sodic-calcic compositions that correspond to ferrichterite, only in the massive facies and predominant sodic compositions including arfvedsonite and riebeckite (Table II). The former is the typical sodic phase in the protomylonitic, massive and microgranitic facies, while the latter predominates in the cataclastic granites. In common, all phases record similar and invariable low *#mg* ($\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$, cationic proportions) parameter values (<0.01 to 0.06). Ti contents are higher in the ferrichterite (up to 2.44 wt. % TiO_2) and arfvedsonite from protomylonitic granites (2.51 wt. % TiO_2), which is also richer in Al (up to 2.08 wt. % Al_2O_3) when compared to crystals from the

massive and microgranitic facies that are also Ca-rich (up to 2.34 wt. % CaO). Maximum Zr abundances are registered in ferrichterite (ca. 0.36 wt. % ZrO_2) and riebeckite (0.44 wt. % ZrO_2) crystals, while F is the primary anion for sodic-calcic and sodic amphiboles, with maximum concentrations of 1.43 wt. % F recorded in arfvedsonite from the protomylonitic facies (Table II).

Figure 4: Rim-core-rim (A-B) analytical profile depicting the main compositional variations in aegirine I crystal from the protomylonitic facies. (i) Photomicrograph under plane polarized light showing concentric and sectorial compositional zoning patterns characterized by green cores with irregular outlines followed by pale-yellow and green irregular intermediate and rim zones. (ii) Back-scattered electron image in compositional mode (BSE-Compo) of the crystal depicted in (i) showing concentric zoning pattern with dark Ti- and Na-rich cores followed by light, Na- and Fe^{3+} -rich intermediate zones and internal rims and Al-rich external rim.

5.2.1. Intracrystal compositional variations

Compositional variations and zoning patterns for a single crystal can be considered similar for sodic-calcic and sodic varieties, though better registered in the arfvedsonite. Figure 5 presents rim-

core-rim zoning profiles for two representative zoned arfvedsonite crystals from the protomylonitic facies that describe the main compositional variations and zoning patterns in the amphiboles of the Papanduva Pluton. Zoning patterns include irregular dark cores with higher Ca and Ti contents and excess of alkalis in the [A] site [$(\text{Na}+\text{K})_{\text{A}} > 1.0$]. These cores are surrounded by intermediate and rim zones registering a progressively Na and Fe^{3+} enrichment parallel to a depletion in Fe^{2+} contents. The [A] also displays excess of alkalis, showing little and concomitant increasing of $(\text{Na}+\text{K})_{\text{A}}$ and Si and decreasing of Al contents, with a consequent increment on the values of the $\text{Na}+\text{K}/\text{Al}$ parameter (Fig. 5, see also Table II).

Figure 6 shows the $\text{Ca}+\text{Al}^{\text{IV}}$ vs $\text{Si}+\text{Na}+\text{K}$ cationic diagram after Giret et al. (1980). Such diagram has been successfully employed to explain compositional variations in amphiboles with only Na and Ca in the [B] site (which excludes the Fe-Mn-Mg amphiboles) from over- and undersaturated silicic rocks (e.g. Strong and Taylor, 1984; Platt and Woolley, 1986; Njonfang and Moreau, 2000; Marks et al., 2004a; Gualda and Vlach, 2007b; Schilling et al., 2011; Reguir et al., 2012). The ferrichterite from the massive facies show restricted variations, though similar to those registered in the sodic amphiboles. Hence, cores are homogeneous, Ca- and Fe^{2+} -rich, with the [A] site partially filled ($\text{Na} + \text{K} < 1.0$)_A. Increasing Na and Fe^{3+} abundances are registered from core to rims, followed by decreasing $(\text{Na}+\text{K})_{\text{A}}$ parallel to Si increment. Consequently, these compositions plot close to the richterite ideal end-member of Figure 6, converging to the arfvedsonite end-member towards crystal rims.

A well-marked compositional difference can be verified between arfvedsonite crystals from the protomylonitic facies and those from the other petrographic facies: in the first case, arfvedsonite shows higher alkali (Na and K) contents which lead to excess in the [A] site. Conversely, the arfvedsonite from the massive and microgranitic facies are more calcic, leading in many cases to partially filled [A] site ($\text{Na}_{\text{A}}+\text{K}_{\text{A}} < 1.0$). As a consequence, the arfvedsonite compositions from the protomylonitic facies span a narrow interval in the diagram of Figure 6 while the others plot between the riebeckite and arfvedsonite end-members. Nevertheless, both cases register compositional trends marked by progressively more sodic compositions towards crystal rims, as verified for ferrichterite.

Figure 5: Rim-core-rim analytical profiles describing the main compositional variations registered in the arfvedsonite crystals from the protomylonitic facies showing irregular, patchy zoning.

Riebeckite is the sodic amphibole in the cataclastic granites and some microgranites. In common. In common, these rocks show subsolidus post-magmatic/hydrothermal alteration features such as secondary albite precipitation, exsolution lamellae and swapped rims in alkali feldspars (cf. Hoshino, 1986; Gualda and Vlach, 2007b), magnetite and hydrothermal zircon (cf. Corfu et al., 2003; Hoskin, 2005) crystallization along rims and fracture planes of amphiboles and clinopyroxenes. Such evidences suggest the formation of riebeckite as result of hydrothermal transformations, replacing primary sodic or sodic-calcic amphibole, following Ernst (1962) who showed that riebeckite is unstable during magmatic stages. Core to rim intracrystal compositional

variations are discrete and vary among different samples. As a whole, variations are characterized by calcic crystal cores with poorly filled (<0.5) [A] site, plotting close to the riebeckite ideal end-member in the diagram of Figure 6. Na and Fe^{3+} contents increase and Fe^{2+} decreases towards crystal rims, similar to compositional trends registered in arfvedsonite and ferririchterite. By the same token, the sum $(\text{Na}+\text{K})_{\text{A}}$ increases parallel to the Si increment, conducting the evolution trends towards more sodic (i.e. arfvedsonitic) compositions.

Figure 6: Cationic diagram $\text{Si}+\text{Na}+\text{K} \times \text{Ca}+\text{Al}^{\text{IV}}$ for amphiboles from the Papanduva Pluton. Blue squares: massive facies; gray circles: protomylonitic facies; inverted green triangles: cataclastic facies; black diamonds: microgranitic facies. Frct: ferririchterite. Arrows describe evolutionary trends from cores to crystal rims.

Compositional variations and evolution trends in amphiboles can also be interpreted in relation to their $[\text{Na}+\text{K}]/\text{Al}$ ratio, which varies according to the host-rock agpaitic index (cf. Giret et al., 1980) as shown in Figure 7. Here, the compositional divergences between the arfvedsonite from the protomylonitic facies and those from the massive and microgranitic facies are strongly depicted. In the first case, evolutionary trends from core to crystal rims are associated to increasing alkalinity and silica over-saturation for the whole data set. In the second case, especially for crystals from the massive facies, arfvedsonite crystallization takes place under conditions progressively more alkaline and silica oversaturated that tend to remain constant close to the crystal rims (Fig. 7). Moreover, similar, yet restricted, evolutionary trends are verified for the riebeckite and ferririchterite (Fig. 7).

Figure 7: Cationic diagram $(\text{Si}+\text{Na}+\text{K}) \times (\text{Na}+\text{K})/\text{Al}$ for amphiboles from the Papanduva Pluton illustrating the alkalinity increase and sílica oversaturation from crystalline core to rims. Rbk: riebeckite. Frct = ferrichterite. Symbols as in Figure 6.

6. TRACE ELEMENT COMPOSITION

A total of ca. 120 trace-element analyses of amphiboles and clinopyroxenes were performed. In order to present an overview of the whole data set and compare the compositional variations inter-phases, we discuss the averages of analyses from the respective minerals, normalized to the primitive mantle values of McDonough and Sun (1995), in the diagrams of Figures 8 to 11, and present the maximum and minimum measured contents of the analyzed trace elements in Tables III and IV.

6.1. CLINOPYROXENES

Average trace (TE) and rare-earth elements (REE) patterns for late-magmatic aegirine I and for post-magmatic aegirine II and aegirine-augite, are shown in Figures 8 and 9, respectively. No aegirine III crystal suitable of ablation experiments were identified in the investigated polished thin-sections. Nevertheless, the data reveal a remarkable difference between compositions for late-magmatic aegirine I from different petrographic facies and mainly between the aegirine and the post-magmatic aegirine-augite.

Table III: Average, maximum and minimum trace element LA-ICP-MS composittions (ppm) for clinopyroxenes from the Papanduva Pluton. b.d.l.: below detection limit. n.a.: not analyzed

Clinopyroxene				aegirine I					
Facies	protomylonitic			cataclastic			microgranitic		
	average	maximum n=16	minimum	average	maximum n=13	minimum	average	maximum n=2	minimum
Li	6.6	28	0.7	6	29	1.2	2.2	3.3	1.1
Be	1.6	1.6	1.6	2.9	5.9	1.4	1.1	1.6	0.6
P	54	91	31	11	31	1.7	14.2	19.7	8.7
Sc	6.5	19	1.1	2.5	4.7	0.5	3.0	4.0	2.1
Ti	9137	26912	854	2199	8384	422	2977	3738	2217
V	1.4	7.4	b.d.l.	0.8	3.0	0.2	0.2	0.3	0.2
Cr	6	16	1.2	1.6	5.8	0.3	1.8	2.5	1.1
Mn	1618	6788	268	269	1445	14	668	975	362
Co	0.5	2.4	0.18	0.04	0.23	b.d.l.	0.1	0.2	0.03
Ni	48	81	0.09	0.04	0.09	0.02	n.a.	n.a.	n.a.
Cu	0.9	3.2	0.05	0.09	0.18	0.04	0.1	0.2	0.1
Zn	1242	8552	189	56	324	2	180.3	263.1	97.5
Ga	8	25	1.8	1.9	8	0.5	3.3	4.8	1.8
Rb	0.07	0.4	b.d.l.	0.2	1.7	0.0	0.3	0.3	0.3
Sr	5.0	13	1.5	1.9	11	0.2	0.5	0.6	0.5
Y	15	46	0.6	25	97	3	26.8	28.7	25.0
Zr	2089	7562	63	748	3297	23	2922.8	3787.0	2058.7
Nb	559	1885	0.0	2.0	5.5	0.2	0.9	1.3	0.4
Mo	1.2	2.2	0.5	0.2	0.5	0.02	0.3	0.3	0.3
Sn	69	233	0.4	31.2	117.8	3.0	21.3	28.1	14.5
Sb	0.1	0.1	0.1	0.01	0.01	0.01	b.d.l.	b.d.l.	b.d.l.
Cs	0.04	0.11	0.01	0.1	0.5	0.0	b.d.l.	b.d.l.	b.d.l.
Ba	0.9	3.3	0.04	0.9	2.5	0.1	0.1	0.1	0.1
La	11	29	1.2	0.8	2.1	0.3	2.0	2.2	1.8
Ce	26	75	4.3	3.0	12.4	1.0	10	11	10
Pr	3.4	10	0.6	0.7	3.4	0.2	2.4	2.8	2.0
Nd	13	41	2.6	4.7	22.7	1.2	14	18	11
Sm	2.5	8	0.4	2.8	16.3	0.9	6	9	4
Eu	0.1	0.3	0.01	0.1	0.7	0.04	0.3	0.3	0.2
Gd	1.4	4.1	0.2	3.5	14.7	1.1	6.1	8.3	4.0
Tb	0.2	0.6	0.03	0.7	3.1	0.2	1.2	1.6	0.8
Dy	1.7	4.7	0.1	5.2	18.2	1.3	7.9	9.6	6.1
Ho	0.6	1.7	0.03	1.0	3.2	0.2	1.7	2.0	1.4
Er	4.2	11	0.3	3.3	10.4	1.0	7.0	7.6	6.4
Tm	1.3	3.7	0.1	0.9	3.2	0.2	2.1	2.4	1.7
Yb	16	50	1.7	11.0	42.5	1.8	26	31	20
Lu	3.6	10	0.5	2.6	11.2	0.4	5	7	4
Hf	40	158	1.4	42.0	204.9	2.8	78	112	43
Ta	43	278	0.7	0.1	0.5	0.01	0.1	0.1	0.04
Pb	0.8	3.2	0.02	0.5	1.4	0.03	0.6	0.8	0.4
Th	0.4	1.7	0.01	0.7	2.8	0.02	0.04	0.04	0.03
U	0.3	0.9	b.d.l.	0.1	0.4	b.d.l.	0.01	0.01	b.d.l.
REE	85	250	12	40	164	16	93	112	73
LREE	56	164	9	12	58	4	36	43	28
HREE	29	86	3	28	106	10	57	69	45
Rb/Sr	0.014	0.031	0.006	0.116	0.857	0.009	0.503	0.496	0.511
Sm/Nd	0.187	0.190	0.167	0.550	0.718	0.372	0.450	0.494	0.376
Y/Ho	0.036	0.042	0.028	26	63	8	0.039	0.039	0.038
La/Y	16	13	14	0.049	0.082	0.009	24	24	26
Zr/Hf	0.155	0.146	0.159	19	36	8	0.194	0.195	0.192
Nb/Ta	7.7	7.8	2.1	50	175	10	7	6	8

Table III: cont.

Clinopyroxene	aegirine I			aegirine II			aegirine-augite (Cpx IV)		
Facies	massive			protomylonitic and massive			massive		
	average	maximum n=6	minimum	average	maximum n=7	minimum	average	maximum n=3	minimum
Li	9.3	16.5	3.6	44	284	1.2	201.4	221.5	162.6
Be	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	19.6	28.2	11.3
P	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	78.8	82.9	72.8
Sc	1.7	2.0	1.2	5	15	2	1.8	1.9	1.6
Ti	4351	8367	329	5736	15833	694	185	218	162
V	3.5	8.8	2.1	4	10	0.1	2.7	3.1	2.1
Cr	0.8	1.6	0.3	2.9	4.2	0.5	12.8	15.1	10.4
Mn	545	756	9	1241	3772	183	60	81	44
Co	0.2	0.4	0.04	0.3	0.7	0.1	0.1	0.2	0.1
Ni	0.1	0.1	0.1	32	42	22	1.2	1.7	0.9
Cu	1.2	3.3	0.0	1.3	9.5	0.0	5.6	8.6	3.7
Zn	55	96	28	380	1165	32	11.7	15.2	8.2
Ga	1.4	3.3	0.2	5	15	0.7	50.7	69.0	38.7
Rb	2.0	10	0.01	8	84	0.01	374.9	495.5	282.5
Sr	6	11	2.3	4.7	12.8	0.8	19.0	22.1	16.3
Y	30	54	15	69	244	2.0	3.6	5.3	2.5
Zr	536	632	446	1075	6447	187	95.7	104.2	82.0
Nb	4.0	9.3	0.1	86	345	0.02	2.4	2.5	2.1
Mo	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5	0.8	0.3
Sn	78	129	20	150.1	518.1	23.8	4.6	5.2	4.1
Sb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.2	1.5	0.9
Cs	0.3	0.9	b.d.l.	0.5	1.9	0.01	32.5	37.6	26.2
Ba	1.9	3.1	0.1	5	48	0.1	174.3	317.0	76.4
La	2.9	3.7	2.2	9	31	0.1	3.6	5.2	2.8
Ce	6	11	3	21	64	0.4	7.4	10.3	5.5
Pr	0.9	1.7	0.3	4	10	0.1	0.8	1.3	0.6
Nd	4	8	1.2	18	45	0.8	3.2	5.0	2.0
Sm	1.1	2.2	0.3	7	23	0.3	0.7	1.0	0.6
Eu	0.1	0.1	0.1	0.3	1.8	0.0	0.1	0.1	0.1
Gd	1.5	2.9	0.5	7	40	0.2	0.6	0.7	0.4
Tb	0.3	0.5	0.1	1.5	9	0.0	0.1	0.1	0.0
Dy	2.8	4.5	1.3	12	70	0.3	0.5	0.7	0.2
Ho	0.8	1.1	0.3	3	13	0.1	0.1	0.2	0.1
Er	3.8	6.2	1.9	12	43	0.4	0.4	0.5	0.2
Tm	1.4	2.4	0.8	3	7	0.2	0.0	0.1	0.0
Yb	25	43	9	30	75	3.1	0.3	0.3	0.2
Lu	7	12	2	6	18	0.9	0.1	0.1	0.0
Hf	36	81	15	32	116	11	2.2	2.6	1.7
Ta	0.4	0.8	b.d.l.	4	27	0.0	3.5	3.8	2.8
Pb	1.0	2.0	0.3	14	62	0.1	14.6	15.3	13.8
Th	1.7	3.9	0.02	3	13	0.0	1.2	1.7	0.9
U	0.05	0.1	b.d.l.	4	21	0.0	0.6	0.6	0.6
REE	58	98	22	133	410	9	18	26	13
LREE	15	26	7	59	162	2	16	23	11
HREE	43	73	16	74	274	5	2	3	1
Rb/Sr	0.350	0.950	0.003	4.140	47.008	0.001	20	22	17
Sm/Nd	0.271	0.297	0.276	0.361	0.662	0.228	0.236	0.195	0.308
Y/Ho	0.086	0.058	0.154	25	38	16	0.120	0.135	0.089
La/Y	17	22	10	0.241	0.828	0.030	6.16	5.53	6.48
Zr/Hf	0.197	0.189	0.234	30	55	11	0.14	0.15	0.11
Nb/Ta	9	8	11	27	57	3	5.7	6.1	5.1

Table IV: Average, maximum and minimum trace element LA-ICP-MS composittions (ppm) for amphiboles from the Papanduva Pluton. b.d.l.: below detection limit.

Amphibole	arfvedsonite			riebeckite			riebeckite			ferrichterite		
Facies	protimylonitic			cataclastic			microgranitic			massive		
	average	maximum	minimum	average	maximum	minimum	average	maximum	minimum	average	maximum	minimum
	n=24			n=2			n=5			n=11		
Li	2653	9711	180	754	1074	433	713	940	553	575	1210	110
Be	4	5	3	6	9	3	7	10	6	40	85	14
P	19	25	16	8	10	6	12	15	9	49	94	30
Sc	5	13	1.0	9	14	5	2	2	1.4	14	34	5
Ti	10540	26670	1102	2792	3813	1772	4057	5231	3233	13684	22009	4654
V	2.3	11	0.1	4.4	6	2.4	0.4	0.5	0.3	21	46	5
Cr	4.4	18	0.7	1.2	1.6	0.8	2.0	2.9	1.5	8	14	3
Mn	2442	5235	20	2582	3577	1587	3113	4151	2333	3934	9490	265
Co	1.0	3.5	0.2	0.5	0.7	0.3	0.4	0.5	0.4	4.8	8.2	0.6
Ni	33	132	0.04	0.08	0.11	0.04	0.06	0.11	0.02	3.1	4.7	1.4
Cu	0.5	1.6	0.03	0.8	1.3	0.3	0.6	0.8	0.4	1.8	15.9	0.3
Zn	3214	10266	434	765	1074	456	1219	1533	1033	1765	3792	433
Ga	8	21	1.6	3	4	1.5	4	5	4	12	21	3
Rb	29	104	4	6	8	4	10	16	8	24	58	4
Sr	14	36	3	10	14	5	4	5	3	37	104	14
Y	62	254	7	60	93	27	57	70	46	184	436	66
Zr	517	1666	91	82	108	56	240	329	191	733	4297	198
Nb	53	310	10	17	23	11	25	35	19	148	498	40
Mo	0.2	0.4	0.1	0.2	0.3	0.1	0.13	0.2	0.1	0.6	0.7	0.5
Sn	21.4	71.9	2.2	4.2	6.1	2.3	6.0	8.3	4.2	31.3	171.1	7.7
Sb	0.05	0.05	0.05	0.03	0.05	0.01	0.04	0.04	0.04	0.2	0.2	0.1
Cs	0.1	0.4	b.d.l.	0.2	0.2	0.1	0.2	0.5	0.1	1.8	12.5	0.01
Ba	1.8	17	0.1	1.3	1.7	0.8	1.3	1.9	0.8	9.7	42.5	1.2
La	7	26	0.8	5	7	3	5	6	4	25	73	14
Ce	18	61	2	13	18	8	15	18	11	57	109	38
Pr	3	11	0.4	2	3	1.5	2	3	2	11	26	6
Nd	12	52	2	12	16	7	11	12	9	48	107	24
Sm	4	25	0.4	4	5	3	4	4	3	14	31	6
Eu	0.12	0.6	0.02	0.2	0.3	0.12	0.14	0.2	0.11	0.6	1.4	0.3
Gd	4	24	0.3	5	8	3	5	5	4	14	32	6
Tb	0.7	3.4	0.1	0.9	1.4	0.5	1.0	1.1	0.9	2.4	5.5	0.9
Dy	6	23	0.8	7	10	4	8	10	7	21	46	9
Ho	2	11	0.2	2	2	0.9	2	3	2	6	13	3
Er	12	72	1.1	6	9	3	10	14	8	34	85	12
Tm	3	22	0.2	1.4	2	0.8	3	3	2	9	27	3
Yb	40	237	3	15	21	9	27	35	21	92	309	35
Lu	9	49	0.7	3	5	2	6	7	5	17	57	8
Hf	17	46	3	2	3	1.4	7	9	6	27	156	8
Ta	1	8	0.2	0	0	0	0	0.9	0	2	8	0.5
Pb	6	40	0.7	5	7	3	12	19	7	35	79	12
Th	0.5	7	0.02	2	3	1.1	1.2	2	0.4	3	16	b.d.l.
U	0.7	3	0.01	0.1	0.1	0.1	0.1	0.2	0.1	0.4	2	b.d.l.
ETR	121	474	20	77	108	46	98	121	82	353	682	203
ETRL	44	175	6	36	50	23	37	44	29	156	347	94
ETRP	77	420	10	40	58	23	61	78	52	197	537	95

The normalized TE concentrations for late-magmatic aegirine I from the protomylonitic granites are characterized by relatively higher Zn and HFSE abundances (Fig. 8A). Such enrichment is extreme for Nb-Ta, up to 1000 times higher than the primitive mantle values, which means abundances of 50 – 1885 ppm and 0.7 – 278 ppm for Nb and Ta, respectively (Fig. 8A; Table III). Conversely, the concentrations of Nb and Ta are two orders of magnitude lower in crystals from the massive granites, to three orders in the microgranites. The latter also reveals aegirine with the highest Zr contents while the massive granites are characterized by aegirine with the highest large ion lithophile elements (LILE) contents (Fig. 8A; Table III). Strong negative peaks for Ba and Sr and for the transition metals V and Co are common to aegirine from all petrographic facies, while relative depletion for Pb and Li is registered for aegirine from the protomylonitic granites and microgranites, respectively (Fig. 8A).

Figure 8: Averaged mantle-normalized trace element (TE) patterns for (A) late-magmatic aegirine I and (B) post-magmatic aegirine II and aegirine-augite.

Normalized average REE patterns for aegirine I (Fig. 9A) are 0.5 to 100 times enriched relative to the primitive mantle values and show a typical V-shape, as in other aegirines elsewhere (Larsen, 1976; Piilonen et al., 1998; Marks et al., 2004a), revealing a pronounced enrichment of HREE ($0.01 \leq \text{La}_N/\text{Yb}_N \leq 2.3$ $0.01 \leq \text{Gd}_N/\text{Yb}_N \leq 0.4$) and a strongly developed negative Eu anomaly ($0.1 \leq \text{Eu}/\text{Eu}^* = \text{Eu}_N/[\text{Sm}_N \cdot \text{Gd}_N]^{1/2} \leq 0.4$). A remarkable difference between the REE patterns can be identified between crystals from the protomylonitic and massive granites relative to the aegirine from

the cataclastic granites and microgranites. For the LREE, aegirine from the protomylonitic facies register higher abundances, mostly for La to Pr and a relative depletion with $0.7 \leq \text{La}_N/\text{Sm}_N \leq 9.4$. Such behavior is also verified for the aegirine from the massive granites, despite the 2 times lower LREE abundances, with $0.1 \leq \text{La}_N/\text{Sm}_N \leq 4.8$. Conversely, in the cataclastic granites and microgranites, aegirine exhibits a steeply-rising slope through the LREE, with $0.1 \leq \text{La}_N/\text{Sm}_N \leq 0.5$. Moreover, the flat patterns between Gd and Dy also differ from the patterns registered in aegirine from protomylonitic and massive granites (Fig. 9A).

Figure 9: averaged mantle-normalized rare-earth element (REE) patterns for (A) late-magmatic aegirine I and (B) post-magmatic aegirine II and aegirine-augite. Symbols as in Figure 8.

Zoning patterns, though coherent for major and minor elements, are inconsistent when it comes to the trace element contents, varying between distinct crystals and samples. Nevertheless, many late-magmatic aegirine I crystals, primarily from the protomylonitic granites, exhibit lower LILE abundances towards crystal rims. HFSE variations are heterogeneous, increasing or decreasing towards different crystal rims and Zn is somewhat invariable (Figs. 8A, 10). Decreasing REE abundances towards intermediate crystal zones and rims are detected, mainly for LREE (Figs. 9A, 10).

The post-magmatic aegirine II shows similar TE and REE patterns (Figs. 8B, 9B). Main differences to the late-magmatic aegirine I are related to higher LILE, Sn and transitional metals abundances. It is worth to note the positive peaks for Th, U and Pb (Fig. 8). This aegirine also registers higher REE contents, with both LREE and HREE relative enrichments ($0.1 \leq \text{La}_N/\text{Sm}_N \leq$

3.0, $0.01 \leq \text{La}_N/\text{Yb}_N \leq 0.4$ and $0.1 \leq \text{Gd}_N/\text{Yb}_N \leq 0.4$) and well developed negative Eu anomaly ($0.04 \leq \text{Eu}/\text{Eu}^* \leq 0.2$). Crystals mantling ferrichterite register higher abundances for most of the elements (e.g. Nb-Ta, REE, Zr-Hf, Rb, Zn).

Figure 10: Zoning profiles for selected trace elements (ppm) from core to rim of a single aegirine I crystal from the protomylonitic facies.

Distinct averaged mantle-normalized TE and REE patterns characterize the post-magmatic aegirine-augite (Figs. 8B, 9B). Most trace elements are depleted by a factor of about 2 to 3 times compared to the late- and post-magmatic aegirine (Fig. 8). Conversely, higher concentrations for the LILE are registered and a strongly developed positive Li anomaly is detected. REE normalized concentrations are up 5 times higher than the primitive mantle values but up to 2 orders of magnitude lower when compared to the aegirines (Fig. 9). The patterns exhibit a steeply-descending slope from the LREE to the HREE. They are flatter, though with some dispersion for the HREE, which may be related to the low measured concentrations (11 – 23 ppm), in many cases close to the instrument detection limits, resulting in a less pronounced negative Eu anomaly ($0.3 \leq \text{Eu}/\text{Eu}^* \leq 0.5$). The relative LREE enrichment over HREE registered for the aegirine-augite ($8 \leq \text{La}_N/\text{Sm}_N \leq 13$) is a diagnostic feature when comparing with the aegirine REE patterns (Fig. 9).

6.2. AMPHIBOLES

Averaged mantle-normalized TE and REE patterns for ferririchterite, arfvedsonite and post-magmatic riebeckite are shown in Figures 11 and 12, respectively. Normalized trace element concentrations are <0.1 to 1000 times higher than the primitive mantle values, while REE normalized concentrations are 1 to 400 times higher.

The arfvedsonite shows higher concentrations for Rb, U and Pb (LILE), Nb, Ta, Zr and Hf (HFSE), as well as Li and Zn, relative to the riebeckite (Fig. 11). REE normalized concentrations are up to 130 times higher than the primitive mantle values. The patterns register enrichment of HREE ($0.03 \leq \text{La}_N/\text{Yb}_N \leq 3.0$), being flat in the LREE region ($0.5 \leq \text{La}_N/\text{Sm}_N \leq 4.0$) and showing a steeply-rising slope through the HREE, with well-developed negative Eu anomaly ($0.1 \leq \text{Eu}/\text{Eu}^* \leq 0.2$) (Fig. 12).

Figure 11: averaged mantle-normalized TE patterns for amphiboles from the Papanduva Pluton. Symbols as in Figure 8.

The riebeckite are depleted in most of the LILE, HFSE and transition metals when compared to the arfvedsonite and ferririchterite, especially (Fig. 11). The REE normalized concentrations are up to 100 times higher than the primitive mantle values and the patterns are almost similar to those for the ($0.7 \leq \text{La}_N/\text{Sm}_N \leq 1.0$ and $0.10 \leq \text{Eu}/\text{Eu}^* \leq 0.14$), though slightly depleted in HREE ($0.1 \leq \text{La}_N/\text{Yb}_N \leq 0.2$), especially from Ho to Lu (Fig. 12)

Lastly, ferririchterite from the massive granites can be distinguished by relative enriched compositions for all elements but Rb, Li and Zn (Fig. 11), as previously verified from the EPMA

analyses (e.g. Ti e Zr) The REE normalized concentrations 3 – 4-fold higher relative to the sodic amphiboles. Patterns are similarly flat for the LREE ($0.6 \leq La_N/Sm_N \leq 4.0$), register a HREE enrichment ($0.1 \leq La_N/Yb_N \leq 1.1$ and a well-defined negative Eu-anomaly ($0.1 \leq Eu/Eu^* \leq 0.2$) (Fig. 12).

Figure 12: Averaged mantle-normalized REE patterns for amphiboles of the Papanduva Pluton. Symbols as in Figure 8.

Figure 13: Zoning profiles for selected trace elements (ppm) from core to rim of a single arfvedsonite crystal from the protomylonitic facies.

Similar to the clinopyroxenes, compositional zoning involving trace elements are inconsistent for amphiboles, with intercrystal and intracrystal variations (Fig. 13). Nevertheless, they can be more evident in many arfvedsonite crystals where decreasing Rb, Sr, Ba (LILE), Y, Zr, Nb and Hf (HSFE), as well as Sn, Li, transition metals and REE contents are verified from core to crystal rims (Figs. 11 to 13).

7. STABLE OXYGEN ISOTOPE DATA

Oxygen isotope ratios for amphiboles and clinopyroxenes separates are presented in Table V and plotted in Figure 14. Some relevant ratios measured in quartz are also presented and will be discussed later. Measuring was conducted on coexisting ferririchterite and aegirine crystals from the massive granites (sample MR-89) and arfvedsonite and aegirine from porphyroclastic coarse-grained alkali-feldspar granite (sample MR-21) and mylonitic, fine-grained alkali-feldspar granite (MR-03), both from the protomylonitic facies. Individual ratios for ferririchterite, riebeckite and aegirine crystals are also available for other massive granite sample (MR-39), microgranites (MR-01D) and cataclastic granites (sample MR-47B), respectively.

Figure 14: Oxygen isotope composition (‰) of mineral separates of the Papanduva Pluton.

Table V: Oxygen isotope ratios (VSMOW, ‰) of mineral separates from the Papanduva Pluton

Facies	Mineral	Sample	$^{18}\text{O}/^{16}\text{O}$	2 σ error
Massive	quartz	MR-89	7.27	0.08
		MR-39	8.39	0.1
	arfvedsonite	MR-89	2.25	0.22
		MR-39	3.34	0.06
	aegirine	MR-89	2.94	0.18
Protomylonitic	quartz	MR-03	10.15	0.12
		MR-21	9.19	0.08
	arfvedsonite	MR-03	4.52	0.2
			5.63	0.08
		MR-21	3.62	0.12
	aegirine	MR-03	6.41	0.08
		MR-04	4.21	0.22
		MR-21	3.03	0.18
Cataclastic	quartz	MR-47B	8.42	0.06
	aegirine		3.77	0.08
Microgranitic	quartz	MR-01D	7.53	0.08
	arfvedsonite		3.73	0.18

Values of $\delta^{18}\text{O}$ span a large range between 2.3 to 6.4 ‰, increasing from the massive to the protomylonitic granites. Ferrichterite registers the lowest values, between 2.3 – 3.3 ‰, while ratios for most of the arfvedsonite, riebeckite and aegirine are similar and vary inside the interval 3.0 – 3.8 ‰. Nonetheless, systematic higher values for the arfvedsonite and aegirine $\delta^{18}\text{O}$ from the highly deformed protomylonitic granite of sample MR-03 were measured. These are between 4.5 – 5.6 ‰ and 4.2 – 6.4 ‰, respectively (Fig. 14).

8. DISCUSSION

8.1. EVOLUTIONARY TRENDS

8.1.1. Clinopyroxenes

Evolutionary trends for clinopyroxenes can be discussed in the ternary diagram Aeg+Jd – NAT+NAZ – Di+Hd of Figure 15, a variant of the diagram presented by Rønsbo et al. (1977), with the NAZ molecule instead of NATAL (NaTiAlSiO_6). Trends for aegirine I and II register systematic NAT+NAZ decreasing and Aeg+Jd towards crystal rims, with constant Hd(+Di). Conversely,

aegirine-augite trends are characterized by an early decreasing of Di and Hd molecule contents towards intermediate crystal zones, with constant NAT+NAZ, followed by decreasing NAT and NAZ contents close to the crystal rims, with constant Di+Hd (Fig. 15).

Figure 16 presents some compositional trends in the ternary diagram Na (Eg) – Mg (Di) – $\text{Fe}^{2+} + \text{Mn}$ (Hd) registered for clinopyroxenes from alkaline granitic and syenitic rocks elsewhere, as well as for other occurrences in the Graciosa Province. In general, evolutionary trends are defined by Mg decreasing and $\text{Fe}^{2+} + \text{Mn}$ increasing, followed by a late increment in the Na contents. The aegirine and aegirine-augite from the Papanduva Pluton are between the most evolved composition within the Graciosa Province, with invariable high Na and low Mg and $\text{Fe}^{2+} + \text{Mn}$ contents (Fig. 16). Their evolutionary trends span a narrow range along the Na (Aeg) - $\text{Fe}^{2+} + \text{Mn}$ (Hd) axis, mainly close to the Aeg apex, and are partially similar to the compositional tendencies registered in A-type granites and microgranites from the Puklen Alkaline Complex, Greenland (Marks et al., 2003), and in quartz syenites and granites from the Pandé Massif, Cameroon (Njonfang and Moreau, 2000). The former show compositions varying from $\text{Eg}_{76}\text{Di}_4\text{Hd}_{20}$ to $\text{Eg}_{92}\text{Di}_0\text{Hd}_8$, while for the latter, a broader compositional interval is registered, between $\text{Eg}_{52}\text{Di}_0\text{Hd}_{48}$ a $\text{Eg}_{100}\text{Di}_0\text{Hd}_0$, under increasing peralkalinity (Fig. 16).

Figure 15: Ternary molecular Eg+Jd – NAT+NAZ – Di+Hd diagram showing the main evolutionary trends from core to rim of clinopyroxenes from the Papanduva Pluton. Agt: aegirine-augite; Eg: aegirine; Jd: jadeite; Di: diopside; Hd: hedenbergite; NAT: $\text{NaTi}_{0.5}(\text{FM})_{0.5}\text{Si}_2\text{O}_6$; NAZ: $\text{NaZr}_{0.5}(\text{FM})_{0.5}\text{Si}_2\text{O}_6$. Symbols as in Figure 6.

Figure 16: Cationic diagram Na – Mg – Fe²⁺+Mn comparing the compositional variations for (A) clinopyroxenes from the Papanduva Pluton and (B) clinopyroxenes from interesting locations worldwide, including other plutons from the Graciosa Province. 1: Pantelleria (pantellerites), Italy (Nicholls and Carmichael, 1969); 2: Oslo Rift (Newmann, 1976); 3: Klokken Syenite, Greenland (Parsons, 1979); 4: Pandé Syenite (Njonfang and Moreau, 2000); 5: Puklen Complex, Greenland (Marks et al., 2003); 6: Ilímaussaq Complex (Larsen, 1976); 7: Nandewar volcano (Abbott, 1969); 8: Serra da Graciosa granites, syenites and monzodiorites, Graciosa Province (Gualda and Vlach, 2007b); 9: Corupá syenites, Graciosa Province (Garin, unpublished data). Symbols as in Figure 6.

1.1.1. Amphiboles

Evolutionary trends for the amphiboles from the Papanduva Pluton are typical of oversaturated peralkaline rocks elsewhere (e.g. Mitchell, 1990; Martin, 2007), and indicate crystallization during late-magmatic stages towards alkali- and silica-rich and Ca- and Al-poor compositions (Giret et al., 1980). They can be compared, at least in part, with the magmatic to subsolidus trajectories of Strong and Taylor (1984), characterized by evolution under reducing environments, with the Fe³⁺/(Fe²⁺+Fe³⁺) ratio close to 0.2. Such scenario does apply for the ferrichterite and the arfvedsonite from the protomylonitic facies, while in arfvedsonite from the massive granites, the values of Fe³⁺/(Fe²⁺+Fe³⁺) ratio are generally higher than 0.2. In fact, in most cases, values are

closer to those registered in the riebeckite from the cataclastic facies (> 0.3), suggesting oxidizing crystallization environments. According to Hawthorne et al. (1993), if the entrance of Li coupled to Fe^{3+} in the [C] is considered during structural formulae calculation, those magmatic to subsolidus trajectories can be equally or even more oxidizing than the so-called “oxidizing trajectories” of Strong and Taylor (1984). Furthermore, as discussed by Marks et al. (2011), at sufficiently high $a\text{Na}_2\text{O}$ the precipitation of arfvedsonite and aegirine can occur in both reduced and oxidized systems.

Figure 17: Cationic diagram $\text{Si+Na+K} \times \text{Ca+Al}^{\text{IV}}$ showing compositional intervals of amphiboles from interesting localities worldwide, including other plutons from the Graciosa Province. (A) Ideal end-members. (B) 1: Oslo Rift (Newmann, 1976); 2: Newfoundland (Strong and Taylor, 1984); 3: Belknap Mountains (Dorais, 1990). (C) 1: Mulanje (Platt and Woolley, 1986); 2: Pandé Syenite (Njonfang and Moreau, 2000); 3: Puklen Complex (Marks et al., 2003). (D) 1: Serra da Graciosa Alkaline Association 1, Graciosa Province (Gualda and Vlach, 2007; 2007c); 2: Serra da Graciosa Alkaline Association 2, Graciosa Province (Gualda and Vlach, 2007b; 2007c); 3: Corupá Pluton, Graciosa Province (Garin, unpublished data). All data were recalculated following the procedures described in Section 3.

Compositional variations and evolutionary trends for amphiboles from various alkaline rocks elsewhere, as well as for other plutons within the Graciosa Province are compiled in the Ca+Al^{IV} vs. Si+Na+K of Figure 17. Comparatively, compositional variations registered for the amphiboles of the Papanduva Pluton, as depicted in Figure 6, are very limited, since typical calcic compositions are lacking, in accordance to the evolved nature of these rocks. Nevertheless, these variations follow the primary magmatic trajectory of Mitchell (1990) as in other peralkaline granitoids elsewhere, characterized by a progressively increasing of the Ca_B contents parallel to Si increasing.

The ferrichterite and arfvedsonite compositions partially overlap those found in the Pandé Massif (Njonfang and Moreau, 2000), those of the “group 3” amphiboles from granites and syenites from the Oslo Rift (Newmann, 1976), where crystallization took place under reduced conditions, and those from syenites of the Corupá Pluton in the Graciosa Province (Garin, unpublished data) (Fig. 17). Conversely, the restricted evolutionary trends registered for the riebeckite of the Papanduva Pluton (Fig. 6) can be partially compared to the variations in sodic amphiboles of the alkaline association 2 of the Serra da Graciosa plutons (Fig. 17; Gualda and Vlach, 2007c). In this case, however, compositions evolve parallel to a decreasing peralkalinity.

1.2. COMMENTS ON THE Ti AND Zr ENRICHMENT IN AEGIRINE

As previously discussed in Section 5.1, Ti and, to a least extent, Zr, are important elements in many aegirine I and II crystals. Many controlling factors have been invoked to explain the Ti and Zr-enrichment in aegirines, such as fluid composition, lacking of concurrent Ti/Zr-bearing phases and the activity of O_2 (e.g. Flower, 1974; Rønsbo et al., 1977; Nielsen, 1979; Piilonen et al., 1998; Mann et al., 2006). The latter, in special, is somewhat contradictory (Dyulgerov and Platevoet, 2006), once

it seems that both high and low fO_2 can favor Ti and Zr entrance into the aegirine structure (e.g. Larsen, 1976; Jones and Peckett, 1980).

Most Ti- and Zr-rich aegirine described in the literature are characterized by an anti-pathetic relation between Ti and Zr (e.g. Wagner et al., 1988; Piilonen et al., 1998; Dyulgerov and Platevoet, 2006). This seems not to be true for the Papanduva Pluton, where Ti and Zr show complex relationships, with both positive and negative correlations from sample to samples, as observed in the aegirine from the Katzenbuckel volcano, Germany (Mann et al., 2006).

Watson (1979), Watson and Harrison (1983), Gwinn and Hess (1989) and Keppler (1993) demonstrate that the excess of alkalis and F increases the Zr and Ti solubility in evolved liquids. Thus, the Ti and Zr entrance into the aegirine structure would be favored in environments with less pronounced peralkalinity. On the whole, aegirines I and II from the Papanduva Pluton register higher Ti and Zr contents closer to Ca-rich core zones, decreasing towards crystal rims, parallel to an increasing in Na and Fe^{3+} contents. Therefore, it seems that, in our case, the alkali activity in the late- to post-magmatic liquids and fluids are the main factor controlling the Ti and Zr enrichment. However, one must also consider the competition with HFSE-bearing accessory minerals that precipitate during these stages, mainly in the protomylonitic granites. Small drop outs in the alkali activity, related to diverse causes, such as fO_2 and pF_2 variations would allow Ti and Zr to be preferentially incorporated into crystal cores. Upon progress of crystallization, increasing peralkalinity stabilizes these and other HFS elements in the crystallizing melts or fluid phases, leading to Ti-poor and Na-rich crystal rims.

2. LATE- TO POST-MAGMATIC EVOLUTION AND PROCESSES

2.1. TRACE ELEMENT PARTITION AND CONTROLS

Amphiboles are magmatic to post-magmatic phases in the Papanduva Pluton, while clinopyroxenes precipitate typically during late-magmatic to post-magmatic stages and no textural evidences suggesting coprecipitation or equilibrium between these minerals are identified. Hence, the any partition coefficient estimates would result in unreliable results, except for those arfvedsonite crystals mantled by aegirine II as will be discussed later. Nevertheless, arfvedsonite

and aegirine share similar evolution trends and compositional variations, in special the Na and Fe^{3+} increasing towards crystal rims. Likewise, some similarities are observed in the trace element compositions, mainly for Rb, Sr, Eu, V-Co, Zr-Hf and REE.

The composition and structure of crystallizing melts or fluid phases and the control by crystal-chemical effects, besides P, T and $f\text{O}_2$ are the main factors that can control the relative trace element abundances in minerals (e.g. Blundy and Wood, 1994; Adam and Green, 2003; Bennet et al., 2003; Marks et al., 2004a; Reguir et al., 2012), as discussed in the previous section for Ti and Zr. On the other hand, as exposed by Marks et al. (2004a), the abundance of a certain trace element in melts may be controlled by factors such as the fractionation of minerals that preferentially incorporate such element. The granites from the Papanduva Pluton are characterized by high alkali feldspar modal abundances (up to 80%). Since Ba, Sr and Eu are preferentially incorporated in alkali feldspar in silicic magmas (White, 2003), the residual magmas from where the amphiboles and clinopyroxenes crystallized are likely to be depleted in those elements. This would explain the strong negative Ba, Sr and Eu anomalies detected for both minerals (e.g. Marks et al., 2004a). Furthermore, negative Eu anomalies are a typical whole-rock signature in the Papanduva Pluton (Vilalva and Vlach, submitted), even with the lack of plagioclase, mineral that primarily controls negative Eu anomalies (Drake and Weill, 1975). Low concentrations of V and Co, as for other transition metals are also a typical chemical feature of these rocks and can be related to the pronounced negative anomalies of these elements in amphiboles and clinopyroxenes, rather than reflecting fractionation of previous mineral phases.

REE patterns for the clinopyroxenes and amphiboles are sinuous, especially for the sodic varieties. Similar patterns are described in alkali syenitic and granitic rocks by Marks et al. (2004a) and in carbonatites by Reguir et al. (2012) who showed that such sinuous patterns suggest that REE are incorporated in two crystallographic sites with different optimal cation radii (cf. Bottazzi et al., 1999) in alkaline melts. For the pyroxene-group minerals, LREE and HREE partition preferentially in the eight-coordinated $^{[8]}\text{M2}$ and in the six-coordinated $^{[6]}\text{M1}$ sites, respectively (Reguir et al., 2012). Thus, the application of the theoretical model of Wood and Blundy (1997) to predict REE partition coefficients and the composition of the liquids in equilibrium with the

investigated sodic and sodic-calcic clinopyroxenes, both typically Na and Fe³⁺-rich, is inappropriate, since this model assumes total incorporation of REE in the eight-coordinated ^[8]M2 (e.g. Blundy and Wood, 1994; Brenan et al., 1995), yielding no reliable results (cf. discussion in Marks et al., 2004a). Textural evidences indicate that aegirine aegirine-augite crystallize always after the amphiboles precipitaton, during late- to post-magmatic stages (see also Mitchell, 1990; Njonfang and Moreau, 2000). In such a scenario, the appearing of a specific clinopyroxene composition and intracrystal chemical variations seems to be mainly influenced by the composition of the peralkaline residual and hydrothermal fluids in equilibrium (e.g. Ferguson, 1978; Grapes et al., 1979), rather than a major crystal-chemical control. The behavior of Na and Ta (e.g. Fig. 8A) illustrates quite well such an interpretation. Inter-mineral partition data available for a variety of mineral paragenesis consistently demonstrate the greater preference of pentavalent HFSE for the amphibole structure (e.g. Chazot et al., 1996; Zack et al., 1997; Marks et al., 2004a; Reguir et al., 2012 and references therein). This can successfully justifies the relatively lower degree of HFSE enrichment in the aegirine I and aegirine-augite from the cataclastic, microgranitic and massive facies, but it is not coherent with the much higher Nb and Ta contents in the aegirine I and II from the protomylonitic facies, sometimes as higher as those found in the amphiboles (Figs. 8A, 10A). In this case, HFSE-rich residual fluids exert a major influence on the clinopyroxene final compositions. This also reinforces the important role played by superimposed late deformational events in promoting the circulation and concentration of HFSE (and other elements) in the late crystallizing melts and residual fluids, as previously suggested by Vilalva and Vlach (2006; 2010) and Vilalva et al. (submitted). According to these authors, relatively high *f*O₂ and alkali and F contents are also typical features of these fluids.

When analyzing the trace element compositions in the aegirine-augite (Figs. 8B, 9B), one must have in mind that the available data were obtained in crystals from the massive facies, since no adequate aegirine-augite crystals (e.g. size, alteration degree) for ablation experiments were found in the investigated samples. However, based on similar textural contests and major compositional variations, it is assumed similar trace element behavior for aegirine-augite from both massive and protomylonitic facies, since it is a post-magmatic phase, admittedly not affected by the late

deformational events. Although the distinct and relatively depleted aegirine-augite TE and REE patterns (Figs. 8B, 9B) can reflect a major crystal-chemical control, it is worth to emphasize the post-magmatic origin of these clinopyroxenes, after the precipitation of aegirine II (and III?) and a variety of rare HFSE- and REE-bearing accessory minerals, mainly in the protomylonitic facies (Unity A of Vilalva and Vlach, 2010), including narsarsukite, britholite, nacareniobsite, turkestanite, elpidite and other (Na, K)-bearing zirconosilicates (e.g. Vilalva and Vlach, 2006; Vilalva and Vlach, 2010; Vilalva et al., submitted). In particular, the zirconosilicates are characterized by high HREE abundances (up to 120,000 ppm) and a strong enrichment of HREE over LREE (Vilalva, 2007; Vilalva et al., unpublished data), which would explain the HREE-depleted patterns for aegirine-augite (Fig. 9B). Additionally, the behavior of Li in the aegirine-augite is also intriguing (Fig. 8B). Marks et al. (2004a) conclude that the Li partition in clinopyroxenes from the Gardar Province (Greenland) is mainly controlled by the composition of the coexisting liquids, showing, however a strong preference for the amphibole structure (e.g. Hawthorne et al., 1993; 1994; see also Section 3 and Fig. 11). The investigated aegirine-augite records a strong positive peak, unlike what is observed for the aegirine I precipitated from late-magmatic melts that have previously fractionated amphiboles (Fig. 8). Hence, at truly post-magmatic stages, with no influence of amphibole fractionation, Li partition preferentially into the aegirine-augite structure.

Among the amphiboles, ferririchterite and arfvedsonite are magmatic phases. TE (Fig. 11) and REE patterns (Fig. 12) show a systematic decreasing of LILE, HFSE, transition metals and REE normalized abundances from ferririchterite to arfvedsonite. In fact, REE in the ferririchterite are 3 times enriched compared to the arfvedsonite (Fig. 12). Marks et al. (2004a) verify a continuous REE, mainly LREE, decreasing from Ca-rich amphiboles and clinopyroxenes from the Ilímaussaq Complex, towards Na-rich compositions. Such trend would be explained by the fractionation of eudialyte, a REE-bearing accessory mineral which is ubiquitous in those rocks. Similarly, the described REE- and HFSE-depletion in the amphiboles from the Papanduva Pluton, especially the magmatic varieties, can reflect the fractionation of late- to post-magmatic accessory minerals that are typically enriched in those elements, such as narsarsukite, britholite, aenigmatite and neptunite. The fractionation of aegirine I was also important as evidenced by the systematic decrease of Sc

concentrations from ferririchterite (up to 34 ppm) to arfvedsonite (up to 13 ppm) (Table III), and within a growing arfvedsonite crystal (up to 13 to 7 ppm from core to rim, Table III) (e.g. Mahood and Hildreth, 1983).

Riebeckite is formed from arfvedsonite during post-magmatic stages in a substitution reaction that demands relatively more oxidizing conditions (e.g. Ernst, 1962), suggesting the fO_2 have also influenced trace element partition.

2.2. THE REPLACEMENT OF AMPHIBOLE BY AEGIRINE II

The substitution of primary arfvedsonite by late aegirine is a well-known phenomenon in peralkaline rocks (e.g. Grapes et al., 1979; Marks et al., 2003). In many cases, increasing of peralkalinity in granitic and syenitic magmas is followed by the lack of Fe-Ti oxides crystallization, specifically within the “no-oxide” field in the T- fO_2 space (Nicholls and Carmichael, 1969), which is, for instance, a common feature in syenitic rocks at the alkaline-peralkaline transition (e.g. Markl et al., 2010). In the “no-oxide” field, Fe-Ti oxides (e.g. ilmenite or magnetite) are unstable phases under the presence of aegirine, arfvedsonite and aenigmatite (Marsh, 1975; Grapes et al., 1979; Marks et al., 2003; Markl et al., 2010). Upon progress of crystallization in such conditions, the Fe^{2+}/Fe^{3+} of the melt increases steadily, giving rise to more reduced conditions during the late magmatic stages, where the peroxidic character of the melts favors the crystallization of arfvedsonite and aegirine to accommodate the available Na in a typical agpaitic crystallization sequence (e.g. Khomyakov, 1995; Sørensen, 1997; Marks et al., 2011). The crystallization of arfvedsonite and aegirine in the absence of Fe-Ti oxides involves reducing reactions such as (Markl et al., 2010):

and

with free oxygen being donated by volatile components in the melt.

The assemblage arfvedsonite + aegirine is not restricted to more reduced conditions. For instance, Marks et al. (2001) show that at sufficiently high aNa_2O , these minerals can precipitate

even to relatively high fO_2 values. Further, at higher $aSiO_2$, aegirine would be stabilized at more reducing conditions with respect to arfvedsonite.

Higher partial O_2 and lower H_2O pressures at relatively high temperatures (600 – 625 °C), can favor aegirine stabilization instead of arfvedsonite, according the following reactions (Deer et al. 1978, Bonin 1986):

or

Many works have interpreted the replacing of arfvedsonite by aegirine as a post-magmatic/hydrothermal event, involving peralkaline residual fluids at relatively high fO_2 and low temperatures (ca. 300 – 450 °C) (e.g. Grapes et al. 1979, Salvi and Williams-Jones 1990, Salvi and Williams-Jones 1996, Schmitt et al. 2000, Scaillet and MacDonald 2001, Marks et al. 2003). In this model, the crystallization of primary anhydrous minerals such as alkali feldspar, olivine, augite and Fe-Ti oxides at more reduced conditions (below or close to the quartz-fayalite-magnetite buffer – QFM) would increase the Na, Fe, Si, halogens and water contents in the residual fluids, which combined to decreasing temperatures due to variations in the redox equilibrium, would cause an increment in the Fe^{3+}/Fe^{2+} ratio of the melts (Grapes et al., 1979). Upon progress of crystallization, now at more oxidizing conditions, primary arfvedsonite is replaced by aegirine containing small inclusions of quartz, fluorite and hematite, according to the following reactions (Marks et al., 2003):

or (Salvi and Williams-Jones, 1996):

The substitution of arfvedsonite by aegirine II is a ubiquitous textural feature in the Papanduva Pluton. Although some aegirine II crystals do contain inclusions of quartz and fluorite, a finding that

could validate the substitutions described by Equations 5 and 6, no hematite or Fe-oxides formation related to this process is detected. Alternatively, Salvi and Williams-Jones (1990) interpret aegirine mantles over amphiboles as a kind of hydrothermal alteration in the presence of a Na- and F- rich and Ca-poor orthomagmatic fluid, as follows:

Furthermore, aegirine can also precipitate from a reaction between arfvedsonite and residual (post-magmatic) fluids, as proposed by Grapes et al. (1979):

or according to Schönerberger et al. (2006):

Reactions described by Equations 7, 8 and 9 can be successfully applied to the Papanduva Pluton case and were simplified by Vilalva (2007) in a single reaction, here invoked to explain the post-magmatic replacing of arfvedsonite by aegirine II, as follows:

Eventually, ferrichterite can be partial to totally mantled by aegirine II in the massive facies. Interesting, the aegirine compositions in this case are somewhat Ca-rich (see section 5.1). Such substitution releases Ca to the coexisting fluids and may justify the Ca-rich compositions of the resulting aegirine II (cf. Vilalva, 2007), according to a reaction:

Additionally, the Ca released by the above reaction can be used to precipitate the post-magmatic aegirine-augite, as well as, HFSE- and Ca-bearing rare accessory minerals, such as turkestanite, nacareniobsite and bastnäsite, at least in the protomylonitic facies.

Figure 18: Averaged mantle-normalized TE (A) and REE (B) patterns for primary amphiboles and replacing aegirine II from the Papanduva Pluton.

Figure 18 compares averaged normalized trace element compositions (Fig. 18A) and REE patterns (Fig. 18B) for the arfvedsonite from the protomylonitic facies and ferrichterite from the massive facies with those recorded for replacing aegirine II crystals, while Figure 19 shows the partition coefficients between these phases, calculated using only crystals from the same sample. Here, it is worth to remember that the aegirine II registers higher abundances for many of the analyzed trace elements with respect to the aegirine I (e.g. Figs 8A, 9A). Figure 18 and 19 reinforce the importance of Equations 10 and 11 and suggest that the amphibole composition controls the

relative enrichment in trace elements of aegirine II, at least for those crystals replacing ferririchterite. Conversely, aegirine II replacing arfvedsonite in the protomylonitic facies records higher REE, HFSE and LILE normalized abundances when compared to the original arfvedsonite (Fig. 18), with the partition coefficients decreasing according to the sequence LILE > HFSE > REE > transitional metals (Fig. 19). Therefore, it seems that the composition of the orthomagmatic fluid in equilibrium with the original arfvedsonite in the protomylonitic granites, as described in Equation 10, played a major role in controlling the final composition of aegirine II in these rocks. Additionally, the increasing HFSE and REE contents, as well as Na, F and other elements in the residual orthomagmatic fluids would be influenced by superimposed late- to post-magmatic deformational events that affected the Papanduva Pluton, especially the granites from protomylonitic facies.

Figure 19: Partition coefficients for (A) trace elements and (B) rare-earth elements between post-magmatic aegirine II and mantled magmatic arfvedsonite from the same sample of the protomylonitic facies.

2.3. TESTING THE ROLE OF DEFORMATION: OXYGEN STABLE ISOTOPE EVIDENCE

Oxygen isotope ratios for amphiboles and clinopyroxenes, as well as quartz (Table V), were used to better understand the role of deformation in the composition of crystallizing residual melts and post-magmatic fluids. Figure 20A shows a plot of the $^{18}\text{O}/^{16}\text{O}$ ratios measured in ferricheterite, arfvedsonite, riebeckite and aegirine I (and II?) crystals against ratios registered in quartz grains from the same samples. A concomitant increase of $\delta^{18}\text{O}$ ratios in quartz (7.3 – 8.4 ‰ to 9.2 – 10.1 ‰), amphiboles (2.3 – 3.3 ‰ to 3.6 – 5.6 ‰) and aegirine (2.9 ‰ to 3.0 – 6.4 ‰) is registered from the massive (samples MR-39 and MR-89) towards porphyroclastic (sample MR-21) and protomylonitic (sample MR-03) granites. Hence, it is suggested that deformation degree is the process of $\delta^{18}\text{O}$ elevation (e.g. O'Hara et al., 1997). A positive correlation between deformation and increasing of $\delta^{18}\text{O}$ is also recorded in quartz phenocrysts from rhyolites by King et al. (1997). Deformational events, mainly dynamic processes, would promote the circulation of moderate $\delta^{18}\text{O}$ fluids resulting in isotopic changes in minerals (e.g. O'Hara et al., 1997; King et al., 1997; Marks et al., 2004b). We calculated oxygen isotope compositions for these fluids in sample MR-03, using to the mineral-water fractionation coefficients of Zheng (1993a, 1993b) at a temperature interval between 600 to 400 °C, comprising late- to post-magmatic crystallization stages. Results agree with the above interpretation and show a broad, yet similar $\delta^{18}\text{O}$ variation, from 3.7 to 8.0 ‰ (5.6 – 8.0 ‰ in relation to quartz compositions and 3.7 – 7.0 ‰ in relation to the arfvedsonite and aegirine).

The measured $^{18}\text{O}/^{16}\text{O}$ ratios were also plotted against the agpaitic index (AI) of the host-granite in the diagram of Figure 20B. For sample MR-03, which has two $\delta^{18}\text{O}$ measurements for different arfvedsonite and aegirine fractions (see discussion below), we used the average $\delta^{18}\text{O}$ values of 5.1 and 5.3 ‰, respectively. Results show good positive correlation between AI and $\delta^{18}\text{O}$ values of arfvedsonite and aegirine ($r^2 = 0.89$), as well as medium correlation between AI and $\delta^{18}\text{O}$ values of quartz ($r^2 = 0.50$).

These evidences confirm the important role played by deformation processes affecting the Papanduva Pluton in the concentration and circulation of residual fluids that are isotopically “heavy” and alkali- (i.e. peralkaline), F-rich (as discussed in section 9.2), with consequent high HFSE and REE contents, from where arfvedsonite, aegirine and rare accessory minerals precipitated (e.g.

Vilalva and Vlach, 2006; 2010; Vilalva et al., submitted). In such a context, aegirine-augite appears at post-magmatic stages after the precipitation of aegirine II and HFSE- and REE-bearing accessory minerals, in a distinct chemical, and possibly isotopic, environment.

Figure 20: Binary diagrams confronting (A) $\delta^{18}\text{O}$ values (‰) of amphiboles and clinopyroxenes separates against $\delta^{18}\text{O}$ values of quartz; and (B) $\delta^{18}\text{O}$ values (‰) of amphiboles, clinopyroxenes and quartz separates against the agpaite indexes of the host-granites. Green symbols: clinopyroxenes; blue symbols: amphiboles.

3. FINAL REMARKS: REDOX CONDITIONS

Sodic and sodic-calcic clinopyroxenes and amphiboles are the main mafic minerals in the peralkaline granites from the Papanduva Pluton, Morro Redondo Complex. Clinopyroxenes include late- to post-magmatic aegirine and post-magmatic aegirine-augite, whereas amphiboles are

magmatic arfvedsonite and ferrichterite and post-magmatic riebeckite. Compositional variations are mainly related to increasing Na and Fe^{3+} parallel to decreasing Ca, Fe^{2+} , HFSE and REE from core to crystal rims, suggesting progressively more peralkaline and oxidizing crystallization conditions.

According to Bailey (1969), aegirine formation during late- to post-magmatic stages indicate relatively higher $f\text{O}_2$, between the QFM and HM (hematite-magnetite) buffers in the presence of water. In fact, Equations 10 and 11 show that precipitation of aegirine II are related to late alkali-rich oxidizing fluids. Charles (1975) showed that ferrichterite is stable under more reducing conditions, typically close to the MW (magnetite-wüstite) buffer, at temperatures around 700 – 750 °C and $P_{\text{fluid}} = 1$ kbar. At higher $f\text{O}_2$ values the maximum thermal stability switches to 535 °C. Additionally, the presence of arfvedsonite coexisting with ferrichterite implies an increasing of $f\text{O}_2$ to values between the MW and QFM buffer, at temperatures < 700 °C (Ernst, 1962; Stolz, 1986). However, the significant Li contents and the relatively high $\text{Fe}^{3+}/\text{Fe}^{2+}$ found in many arfvedsonite crystals suggest that this amphibole was stable to even more oxidizing conditions, above the QFM buffer (cf. Marks et al., 2003; Pe-Piper, 2007). Moreover, high F contents in the coexisting melts can also elevate the thermal stability of this mineral (Ernst, 1962; Stolz, 1986; Scaillet and MacDonald, 2001; Marks et al., 2003). Thermometric estimates based on the quartz-mineral equilibrium for various samples from the Papanduva Pluton yielded variable values, many of them inconsistent with the textural and petrologic evidences. This should be related, in part, to the typical agpaite crystallization sequence followed by these rocks, where mafic minerals appear much later than quartz. Hence, these minerals cannot be considered in stable isotopic equilibrium. Despite of that, estimates obtained for two distinct aegirine fractions from sample MR-03, based on the equilibrium quartz-aegirine, according to the fractionation coefficients of Chiba et al. (1989), yielded temperatures of 585 and 426 °C. These values agree with previous results obtained by Vilalva (2007; see also Vilalva and Vlach, submitted and Vilalva et al., submitted) and can be considered good estimates for the temperature interval during late- to post-magmatic crystallizations stages. Late-magmatic temperatures of 585 °C indicate crystallization within the “no-oxide” field for $\log f\text{O}_2$ values of ca. -20 and -19, closer to the QFM buffer, while post-magmatic temperatures of 426 °C

are concordant with the temperature estimates for the replacing of arfvedsonite by aegirine in many localities (e.g. Nicholls and Carmichael, 1969; Grapes et al., 1979; Ike, 1985; Salvi and Williams-Jones 1996, Schmitt et al. 2000, Njonfang and Moreau, 2000; Scaillet and MacDonald, 2001; Marks et al., 2003, Markl et al., 2010).

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ANEXO:

D

NACAREBIOSITE-(Ce) AND BRITHOLITE-(Ce) IN PERALKALINE GRANITES FROM THE MORRO REDONDO COMPLEX, GRACIOSA PROVINCE, SOUTHERN BRAZIL: OCCURRENCE AND COMPOSITIONAL DATA

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ABSTRACT

Textural and chemical (major, minor and trace element) data are reported here for nacarebiosite-(Ce), $\text{Na}_3\text{Ca}_3(\text{REE})\text{Nb}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, and britholite-(Ce), $(\text{Na,Ca,REE})_{10}(\text{Si,P})_6\text{O}_{24}(\text{OH,F})_2$, minerals formed during the late stages of crystallization for the most evolved peralkaline granites from the Morro Redondo Complex, Graciosa Province (Southern Brazil). The nacareniobsite-(Ce) compositions are very close to ideal compositions, with Na_2O and Nb_2O_5 contents up to 11.1 and 15.5 wt. %, respectively, corresponding to an average formula of $\text{Na}_{3.0}(\text{Ca}_{2.75}\text{Sr}_{0.01})_{2.76}(\text{REE,Y})_{1.16}(\text{Nb}_{0.95}\text{Ta}_{0.02}\text{Ti}_{0.04})_{1.01}\text{Si}_{3.99}\text{O}_{14}(\text{O}_{1.11}\text{F}_{2.89})_4$. Compared to the host rock composition, trace-element patterns for nacareniobsite-(Ce) indicate enrichment in REEs, Y and Sr, and depletion in alkali metals and Zr. The chemical data are in excellent agreement with a complete solid solution series between rinkite and nacareniobsite-(Ce) and controlled by the coupled $[\text{M}^{+4}\text{M}^{2+}]_1[\text{M}^{5+}\text{Na}^+]_1$ and, in part, $[\text{M}^{2+}]_2[\text{REE}^{3+}\text{Na}^+]_1$ exchange vectors. The britholite-(Ce) compositions are amongst the most (REE, Y)-enriched reported to date, with REE+Y contents up to 73.6 wt. % oxide. REE and trace element distributions relative to the host rock exhibit some similarities with those observed for nacareniobsite-(Ce); however, Ba, Th, U, and Pb contents are higher. The compositions documented here agree very well with the coupled $[\text{PM}^{2+}\text{F}]_1[\text{Si}(\text{REE,Y})(\text{OH})]_1$, $[\text{M}^{2+}]_2[\text{Na}(\text{REE,Y})]_1$ and $[\text{M}^{2+}(\text{Th,U})]_1[(\text{REE,Y})]_2$ vectors. Crystallization of both minerals was favored by the F-, Na- and HFSE- enriched nature and moderate-to-strong peralkaline signature of the melt

present during the late stages of crystallization at temperatures of $\leq 600^{\circ}\text{C}$ in a relatively reduced environment.

Keywords: nacareniosite-(Ce), britholite-(Ce), EPMA and LA-ICP-MS analysis, peralkaline granites, Morro Redondo Complex, Graciosa Province

1. INTRODUCTION

Nacarenioibsite-(Ce), a sorosilicate with the ideal formula $\text{Na}_3\text{Ca}_3(\text{REE})\text{Nb}(\text{Si}_2\text{O}_7)_2\text{OF}_3$, was discovered by Petersen et al. (1989) in lujavrites from the Ilímaussaq alkaline complex, South Greenland (see also Pekov & Ekimenkova, 2001). It is a very rare mineral, described in some detail only in three other occurrences of alkaline undersaturated rocks in the world: Mecsek Mountains (Nagy, 2003), Los Isle, Guinea (Parodi & Chevrier, 2004) and in the Kilombe volcano, Quenia (Ridolfi et al., 2006). The first occurrence of nacarenioibsite-(Ce) in oversaturated rocks was reported by Vlach & Vilalva (2007) within protomylonitic peralkaline granites from the Morro Redondo Complex, Southern Brazil. The $P2_1/a$ space group symmetry was assigned by the first authors to the holotype species; however, based on an investigation of a sample from the same locality, Sokolova & Hawthorne (2008) concluded that the nacareniosite-(Ce) structure belongs to the $P2_1/c$ space group. The latter also classified it as a Group-I mineral with the so-called TS (titanium silicate) block (see also Sokolova, 2006), with its corresponding general, structural formula of $\text{A}^{\text{P}}_2\text{M}^{\text{H}}_2\text{M}^{\text{O}}_4(\text{Si}_2\text{O}_7)_2\text{X}^{\text{O}}_4$. Sokolova and Hawthorne (2008) state that this is the only mineral with a pentavalent cation that is dominant at one ($\text{M}^{\text{O}}_{(1)}$) amongst the M^{O} sites within the O sheet constituting these blocks.

Britholite was first described by Winther (1901) and is a (REE)-rich mineral with the general formula $(\text{Na,Ca,REE})_{10}(\text{Si,P})_6\text{O}_{24}(\text{OH,F})_2$, with $\text{Si} > \text{P}$ (Oberti et al., 2001). It often forms important economic deposits and is relatively common in alkaline, specially undersaturated rocks, and in some granites, pegmatites, as well as in several related metasomatites (e.g., Fleischer & Altschuler, 1986; Arden & Halden, 1990; Oberti et al., 2001; Pekov et al., 2007). Britholite was considered to be isostructural with apatite and has been classified as both apatite, or belonging to an independent

mineral group (Gaines et al., 1997; Strunz & Nickel, 2001; Pan & Fleet, 2002). In the latter case, these are subdivided into two series (Pekov et al., 2007): the britholite *stricto sensu* series, with $\Sigma(\text{ETR}) > \text{Ca a.p.f.u.}$, and the calciobritholite series, in which $\Sigma(\text{ETR}) < \text{Ca a.p.f.u.}$ Both these series include relatively F-rich species, namely fluorbritholite and fluorcalciobritholite (Gu et al., 1994; Pekov et al., 2007). According to Oberti et al (2001), the structure of britholite-(Ce) is better defined as 6_3 rather than as the $6_3/m$ space group, which is typical of apatite and fluorcalciobritholite (Pekov et al. 2007). Based on Oberti et al (2001), the britholite-(Ce) structure is characterized by one tetrahedral, one $(\text{REE})_2$ unique site and two independent $(\text{REE})_1$ and $(\text{REE})_{1a}$ degenerated sites.

Among the peralkaline granites associated with the A-type granites and syenites from the Neoproterozoic Graciosa Province, Southern Brazil (Gualda & Vlach, 2007), some of the most evolved types that crop out in the Morro Redondo Complex are unique and particularly interesting from a mineralogical perspective. These contain several rare Ti-, HFSE- and REE-bearing minerals, which define agpaitic-like parageneses, formed, with some exceptions, in the late- to post-magmatic crystallization stages. With the exception of several yet poorly described or even unidentified minerals, those that have been reported include: chevkinite, allanite, aenigmatite, astrophillite, narsarsukite, nacarebiosite-(Ce), britholite-(Ce), REE-rich turkestanite, neptunite, elpidite and other (Na,K) zirconosilicates and bastnäsite (Vilalva, 2007; Vlach & Gualda, 2007; Vlach & Vilalva, 2007, Vilalva & Vlach, 2010).

Following the preliminary, previous work of Vilalva & Vlach (2010) and Vlach (2012), this study reports detailed and combined new textural and compositional (EPMA, LA-ICP-MS) data for nacareniobsite-(Ce) and britholite-(Ce) from peralkaline granites (Morro Redondo Complex), and these are compared to available literature data. The main objectives are to contribute to the knowledge of the variations in their major and trace element contents, and to the mineralogical description of the Graciosa Province as a whole. This investigation also attempts to formulate appropriate constraints for future petrological work, in particular with regards to the behavior of the large ion lithophile elements (LILEs) and high field strength elements (HFSEs) during the magmatic and post-magmatic evolution of A-type melts.

2. GENERAL BACKGROUND

The Morro Redondo Complex covers an area of ~250 km² and is one of the largest occurrences of A-type granites and syenites in the Graciosa Province (Gualda & Vlach, 2007; Vilalva & Vlach, 2010). This Neoproterozoic magmatic province was emplaced under an extensional tectonic environment that characterized the evolution of Gondwana in this region of the globe at ca.580 Ma (Vlach et al., 2011). The Morro Redondo Complex consists of typical bimodal basic and acid volcanism, with the two main intrusive units being the Papanduva and Quiriri Plutons. The former pluton is smaller and consists of a variety of peralkaline alkali-feldspar granites (Alkaline Association), whereas the latter contains aluminous, subalkaline, mainly biotite syenogranites (Aluminous Association; Gualda and Vlach, 2007). General background geology and petrography concerning the Morro Redondo complex may be found in Vilalva & Vlach (2010); additional details, in particular relating to the geochemical aspects of the complex are presented in Vilalva & Vlach (submitted).

The location of the sample selected for this work (MR-02 and MR-02A, both with nacareniobsite-(Ce)) is given in Vilalva & Vlach (2010, Fig. 1); that for britholite-(Ce)-bearing sample MR-03 was proximal (~650 meters) to the former. These samples are representative of the white-to-gray protomylonitic petrographic facies (unit A of Vilalva & Vlach, 2010), which crops out at the NE-N-NW borders of the Papanduva Pluton, and characterized by well-developed late-magmatic to solid-state deformational planar structures. Millimetric- to centimetric-sized vugs or miarolitic cavities, sometimes partially filled in with post-magmatic minerals, are also common features.

In this petrographic facies, rounded to irregular alkali-feldspar, arfvedsonite and rare quartz porphyroclasts (up to 4.0 mm) occur in a fine-grained granoblastic matrix made of quartz, microcline, albite, aegirine, some arfvedsonite, and several rare accessory minerals (listed earlier). These samples formed following an agpaitic-like crystallization sequence, where the mafic and accessory minerals began to crystallize after the felsic minerals. Some mafic and most of the rare accessory minerals were, in fact, formed during late- to post-magmatic crystallization stages (e.g. Vilalva & Vlach, 2010; Vilalva et al., submitted). The modal abundances of mafic phases in the studied samples are up to 10% and up to 4% of rare accessory phases.

The geochemical signatures of these alkali feldspar granites are, in short, typical of A-type evolved peralkaline granites documented elsewhere, with high $fe\#$ numbers [$FeO^T/(FeO^T + MgO)$, wt.% oxides] and Agpaitic Indexes $[(Na_2O+K_2O)/Al_2O_3]$, up to 0.99 and 1.30 molar], respectively, as well as relatively high abundances of alkali metals and HFS elements. As expected, abundances for most HFSEs indicate well-defined positive correlations with the Agpaitic Index. All samples yield low magnetic susceptibilities ($< 10^{-3}$ SI) and many of them may be classified as high heat production (HHP) granites, with heat production per unit volume up to $5.7 \mu Wm^{-3}$ (Vilalva & Vlach, submitted).

3. ANALYTICAL METHODS AND DATA TREATMENT

Compositional data for selected nacareniobsite-(Ce)- and britholite-(Ce)-bearing samples were obtained on 30-80 μm thick polished-thin rock sections by EPMA analysis at the Electron Microprobe Laboratory at the Geosciences Institute of the University of São Paulo, Brazil, and LA-ICP-MS analysis at the MITERAC Facility, University of Notre Dame, USA.

3.1. ELECTRON-PROBE MICROANALYSES

WDS analyses were obtained using a JEOL-JXA8600S equipped with 5 wavelength and 1 energy dispersive spectrometers and automated by the Thermo-Noran Voyager 4.3.1 system. Operating conditions were 15 kV, 20 nA, and 5-10 μm for the column acceleration voltage, beam current and diameter, respectively. BSE compositional imaging was systematically used to monitor crystal compositional variations not detected in thin sections and to select analytical spots. The analyzed elements and their set-up were chosen after precise qualitative WDS scans over typical nacareniobsite-(Ce) and britholite-(Ce) grains. The quantified spectral lines, analyzer crystals and used standards for nacareniobsite-(Ce) were: $SiK\alpha$ (PET, Osumilite), $ZrL\alpha$ (PET, ZrO_2 shyntetic), $ThM\alpha$ (PET, ThO_2 synth), $TiK\alpha$ (LIF, titanite), $AlK\alpha$ (TAP, YAIG shynt), $LaL\alpha$, $CeL\alpha$, $PrL\beta$, $NdL\beta$, $SmL\beta$, $GdL\beta$ and $DyL\beta$ (LIF, $(REE)PO_4$ synth, Jarosewich & Boatner, 1991), $YL\alpha$ (PET, YAIG shynt), $FeK\alpha$ and $MnK\alpha$ (LIF, Mn-olivine), $CaK\alpha$ (PET, titanite), $SrL\alpha$ (PET, $SrTiO_3$ synth), $BaL\alpha$ (PET, $BaAl_2Si_2O_8$ synth), $NaK\alpha$ (TAP, jadeite), $NbL\alpha$ (PET, Nb met), $TaL\alpha$ (LIF, Ta met) and $FK\alpha$

(TAP, F-apatite). Similar settings were used for britholite; however, Zr, Ti, Mg, Sr, Nb and Ta were not analyzed, while UM β (PET, UO₂ synth), YbL α (LIF, YbPO₄), PK α (PET, CePO₄) were added to the analytical routine, and BaAl₂Si₂O₈ synth was used as the main Si standard. Total count times, equally divided between peak and background measurements, were variable from 5 for the lightest to 80s for the heaviest elements present in small contents. The PROZA program (e.g. Bastin & Heijligers, 1990) was used for matrix effects correction and data reduction. Spectral interferences of Ce over F and Th over U were corrected as described by Vlach (2010). The estimated relative analytical precision, checked against standards, is better than 2% and up to 10% for the major and minor elements, respectively, and ≤ 0.01 wt.% oxide for the trace elements.

Structural formulae were computed on the basis of 18 (O + F) for nacareniobsite-(Ce) and 26 (O,F) for britholite-(Ce), following Cámara et al. (2011) and Oberti et al. (2001), respectively.

3.2. LASER ABLATION - INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Trace element abundances were determined using a ThermoFinnigan high resolution Element2 ICP-MS instrument coupled to a ESI-New Wave Research UP213 laser ablation system. Selection of spots for laser ablation analysis were based on the most homogeneous areas within crystals as noted in the BSE images; however the spatial resolution of the analysis is lower (30 μ m) as compared with EPMA (5-10 μ m) and consequently the total volumes sampled are much higher for the former. Ablation experiments were carried out using an energy fluence of ~ 10 J/cm², repetition rate of 4 Hz, and spot size of 30 μ m. The He flow rate within the laser ablation cell was ~ 0.70 L/minute. Total acquisition time was 120s, which was equally divided between background and laser ablation ion signal measurements (8 ms dwell time for each isotope), and followed by ~ 30 s of washout time. The following isotopes were measured for both minerals: Li⁷, Ca⁴³, Sc⁴⁵, Ti⁴⁹, V⁵¹, Cr⁵², Mn⁵⁵, Co⁵⁹, Ni⁶⁰, Cu⁶⁵, Ga⁷¹, Rb⁸⁵, Sr⁸⁸, Y⁸⁹, Zr⁹⁰, Sn¹¹⁸, Cs¹³³, Ba¹³⁷, Sm¹⁴⁷, Eu¹⁵¹, Gd¹⁵⁵, Tb¹⁵⁹, Dy¹⁶³, Ho¹⁶⁵, Er¹⁶⁶, Tm¹⁶⁹, Yb¹⁷³, Lu¹⁷⁵, Hf¹⁷⁹, Ta¹⁸¹, Pb²⁰⁸, Th²³² and U²³⁸. Further, Zn⁶⁶, La¹³⁹, Ce¹⁴⁰, Pr¹⁴¹ and Nd¹⁴³; Be⁹, Mg²⁵ and Nb⁹³ were also measured for nacareniobsite and britholite, respectively. The NIST SRM 612 glass was used as the main external standard, while Ca contents

obtained by EPMA were employed as internal standards. Data reduction and elemental abundance determinations were achieved using the Glitter software (van Achterbergh et al., 2001). Overall, the relative analytical precision for all the elements investigated here is in 5-10% (at 95 % confidence level).

Figure 1. Transmitted light and BSE compositional images for nacareniobsite-(Ce) from peralkaline granite (sample MR-02), Papanduva Pluton, South Brazil. **A:** platy, subidiomorphic crystal, under plane polarized light; **B:** fibrous lathy crystals and prismatic crystals, under crossed polarizer's; **C:** BSE image of the crystal depicted in A, showing typical patchy zoning and clear internal areas constituted by unidentified Nb-rich unidentified phases. Ncr, nacareniobsite-(Ce); contrasted textural generations Ncr1 (fibrous) and Ncr2 (prismatic); Qtz, quartz, Kfs, K-feldspar.

4. MICROSCOPY AND TEXTURAL ENVIRONMENT

Nacareniobsite-(Ce) occurs in the matrix of several peralkaline granites samples exhibiting protomylonitic textures (Unit A of Vilalva & Vlach, 2010). It is associated with quartz, microcline and albite in a granoblastic textural arrangement with some arfvedsonite and aegirine as thin prismatic

crystals. Crystal dimensions are typically small (< 1.0 mm). Two main textural generations are recognized: the first is idiomorphic to subidiomorphic, platy to prismatic isolated, and somewhat fractured crystals; the second, of late crystallization origin consists of fibrous aggregates made up of thin crystal laths (Figs. 1A, 1B); the latter typically over grow the neighboring larger crystals. Under transmitted light, the first generation nacareniobsite-(Ce) crystals are transparent, homogeneous, and display both high relief (in relation to the felsic minerals) and a third-order red interference color. A subtle pleochroism, from colorless to very light pink may be seen in some sections, and this feature serves to contrast nacareniobsite-(Ce) from colorless to very light green aegirine thin crystals. BSE compositional imaging reveals that in general nacareniobsite-(Ce) is characterized by remarkable patchy zoning, as well as minute internal irregular areas with higher back-scattered coefficients consisting of unidentified Nb-rich phases (Fig. 1C).

Figure 2. Transmitted light and BSE compositional images for britholite-(Ce) from the peralkaline granite (sample MR-03), Papanduva Pluton, South Brazil. **A:** image of a near (0001) section under plane polarized light; note the broken appearance of the crystal. **B:** BSE image of crystal, showing discrete zoning nature and spongy-textured left rim, indicated by the arrow, in which britholite-(Ce) is partially substituted by bastnäsite. Brt, britholite-(Ce); Qtz, quartz; Kfs, K-feldspar.

Britholite-(Ce) appears mostly as idiomorphic, isolated and typically broken crystals (between 0.1 and 0.3 mm) that exhibit typical hexagonal basal sections that resemble common apatite (Fig. 2A), and is associated with quartz and alkali feldspars. Crystals are homogeneous, uniaxial (-), colorless to creamy-colored, exhibit high relief and a typical anomalous low-order, bluish

to grayish interference color. BSE images display discrete compositional zoning. Some crystals show a spongy-like texture at their most-external rims, and represent alteration and partial substitution of britholite-(Ce) for bastnesite through dissolution-precipitation-like processes occurring in a late hydrothermal event (Fig. 2B).

Petrographic textures indicate that both minerals formed after the deformation of quartz and recrystallization of alkali-feldspar. Of note, despite the fact that both nacareniobsite-(Ce) and britholite-(Ce) occur in the same granite (petrographic) unit from samples located proximal to one another in the field, britholite-(Ce) was not observed in any of the nacarebiosite-(Ce)-bearing samples.

5. COMPOSITIONAL VARIATIONS

Representative major element compositions and structural formulae for nacarebiosite-(Ce) and britholite-(Ce) are listed in Tables 1 and 3, while trace element abundances are reported in Tables 2 and 4, respectively. The main geochemical signatures and compositional variations of these two minerals are discussed relative to available data from other known occurrences (cf. Tables 1, 3). The main reason being that, in general, compositional data from single occurrences do not exhibit significant variation, which then does not allow for a statistical analysis of possible cation exchange reactions involved with the formation of both minerals.

Table 1. Representative WDS compositions (wt. %) and structural formulae for nacareniobsite-(Ce) and rinkite. Structural formulae computed according to Sokolova & Hawthorne (2008). Point_ID: crystal/spot identification, p: platy crystal, f: fibrous, c: core, i: intermediate, r: rim (our data, sample MR-02). Other analyses: A: Petersen et al. (1989): Sokolova & Hawthorne (2008), C: Ridolfi et al. (2006), D: Pekov & Ekimenkova (2001), E: Cámara et al. (2011), F: “mosandrite” (Sokolova & Cámara, 2008). (*): mean analyses. b.d.: below detection limit, n.r.: not reported.

Mineral	Nacareniobsite-(Ce)												Rinkite		
Point_ID	p.1_r	p.5_i	p.7_i	p.8_c	p.9_i	p.11_i	f.2_i	f.1i	A*	B	C	D	A	E	F
SiO ₂	28.34	28.44	28.28	28.43	28.14	28.31	28.15	28.24	29.63	28.30	29.54	29.00	29.18	29.36	29.78
TiO ₂	0.38	0.15	0.16	0.19	0.28	0.18	0.89	0.44	2.79	2.24	1.99	2.01	5.37	8.21	8.47
ZrO ₂	b.d.	b.d.	b.d.	b.d.	b.d.	0.05	0.04	0.04	n.r.	n.r.	0.26	0.04	0.63	0.62	0.79
Al ₂ O ₃	b.d.	b.d.	b.d.	b.d.	b.d.	0.02	0.02	b.d.	n.r.	n.r.	n.r.	0.03	n.r.	n.r.	b.d.
FeO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.07	b.d.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
MnO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.02	0.05	n.r.	n.r.	0.24	n.r.	n.r.	0.13	n.r.
CaO	18.56	18.25	18.67	18.72	18.31	19.17	17.05	19.07	19.92	19.79	20.35	16.88	23.00	24.43	27.06
BaO	b.d.	0.09	b.d.	0.11	0.03	b.d.	0.08	0.05	n.r.	n.r.	n.r.	n.r.	n.r.	0.10	n.r.
SrO	0.11	0.04	0.16	0.10	0.10	0.12	0.07	b.d.	0.27	0.45	n.r.	n.r.	n.r.	1.73	0.26
Na ₂ O	11.10	11.06	11.00	11.10	10.92	11.07	11.03	10.96	10.01	10.07	8.29	10.57	9.38	8.37	7.59
La ₂ O ₃	2.68	2.87	2.76	2.90	2.29	2.06	3.10	2.84	4.09	4.42	4.54	3.19	2.64	3.56	3.14
Ce ₂ O ₃	9.55	9.73	9.54	8.81	10.00	9.13	11.59	10.50	10.32	10.55	9.19	10.34	8.62	9.00	8.36
Pr ₂ O ₃	1.62	1.65	1.70	1.74	1.29	1.62	1.71	1.63	1.42	1.12	1.51	1.35	1.36	1.01	0.85
Nd ₂ O ₃	6.40	6.55	6.17	6.80	5.59	6.07	5.98	4.56	4.19	4.34	3.49	5.57	5.33	3.58	2.58
Sm ₂ O ₃	1.43	1.32	1.27	1.06	1.11	1.19	1.21	0.77	0.81	0.64	0.61	0.83	0.98	0.58	0.40
Gd ₂ O ₃	0.77	0.97	0.52	0.41	0.78	0.63	0.65	0.60	n.r.	0.47	1.11	n.r.	n.r.	0.52	n.r.
Dy ₂ O ₃	0.15	0.15	0.35	0.30	0.14	0.27	0.16	0.11	0.05	n.r.	n.r.	n.r.	0.03	0.41	0.30
Y ₂ O ₃	0.22	0.15	0.31	0.34	0.21	0.35	0.53	0.30	0.78	0.57	1.76	0.48	1.07	1.83	1.79
ThO ₂	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	b.d.	0.08	n.r.	n.r.	n.r.	0.03	n.r.	1.12	0.00
Nb ₂ O ₅	14.92	15.20	15.47	15.15	14.94	15.30	14.00	15.22	11.61	12.01	9.42	12.03	6.63	1.89	1.34
Ta ₂ O ₅	0.53	0.43	0.35	0.48	0.35	0.52	0.60	0.46	0.34	0.33	n.r.	n.r.	0.26	n.r.	0.07
F	6.43	6.35	6.79	6.73	6.52	6.53	6.02	6.51	6.87	6.15	5.62	6.22	6.57	6.47	7.48
O≡F	2.71	2.67	2.86	2.83	2.75	2.75	2.53	2.74	2.89	2.59	2.37	2.62	2.77	2.72	3.15
Sum	100.50	100.74	100.65	100.57	98.30	99.86	100.42	99.70	100.21	98.86	95.55	95.95	98.28	100.20	97.11

Table 1. cont.

Structural Formulae [(O+F) = 18 a.p.f.u.]

Mineral	Nacareniobsite-(Ce)												Rinkite		
ID	p.1r	p.5i	p.7i	p.8c	p.9i	p.11i	f.2i	f.1i	A*	B	C	D	A	E	F
Si	3.993	4.010	3.966	3.987	4.017	3.984	4.015	3.978	4.075	4.014	4.273	4.180	4.040	4.016	4.033
Al	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000
ΣT	3.993	4.010	3.966	3.987	4.017	3.987	4.017	3.978	4.075	4.014	4.273	4.185	4.040	4.016	4.033
Nb	0.950	0.969	0.981	0.961	0.964	0.973	0.903	0.969	0.722	0.770	0.616	0.784	0.415	0.117	0.082
Ta	0.020	0.016	0.013	0.018	0.014	0.020	0.023	0.018	0.013	0.013	0.000	0.000	0.010	0.000	0.003
Ti	0.040	0.016	0.017	0.020	0.030	0.019	0.095	0.046	0.289	0.239	0.216	0.218	0.559	0.845	0.863
Zr	0.000	0.000	0.000	0.000	0.000	0.004	0.003	0.003	0.000	0.000	0.018	0.003	0.043	0.041	0.052
$\Sigma M^{(1)}$	1.011	1.002	1.011	0.998	1.008	1.016	1.024	1.036	1.023	1.022	0.851	1.005	1.026	1.003	0.999
Na	3.008	2.983	2.962	2.986	2.944	3.012	2.975	2.976	2.669	2.769	2.325	2.713	2.518	2.220	1.993
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.058	0.197	0.391	0.000	0.442	0.831	0.845
$\Sigma M^{(2,3)}$	3.008	2.983	2.962	2.986	2.944	3.012	2.975	2.976	2.727	2.966	2.717	2.713	2.960	3.051	2.838
Na	0.024	0.041	0.029	0.032	0.079	0.009	0.075	0.017	0.000	0.000	0.000	0.241	0.000	0.000	0.000
Ca	2.802	2.757	2.806	2.813	2.801	2.891	2.605	2.878	2.877	2.810	2.763	2.607	2.969	2.750	3.081
FeII	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.006	0.000	0.000	0.029	0.000	0.000	0.015	0.000
Ba	0.000	0.005	0.000	0.006	0.002	0.000	0.004	0.003	0.000	0.000	0.000	0.000	0.000	0.005	0.000
Sr	0.009	0.003	0.013	0.008	0.008	0.010	0.005	0.000	0.022	0.037	0.000	0.000	0.000	0.137	0.020
$\Sigma M^{(+1,+2)}$	2.834	2.806	2.848	2.859	2.889	2.909	2.701	2.903	2.898	2.847	2.792	2.848	2.969	2.907	3.101
Dy	0.007	0.007	0.016	0.014	0.006	0.012	0.007	0.005	0.002	0.000	0.000	0.000	0.001	0.018	0.013
Gd	0.036	0.045	0.024	0.019	0.037	0.029	0.031	0.028	0.000	0.022	0.053	0.000	0.000	0.024	0.000
Sm	0.069	0.064	0.061	0.051	0.055	0.058	0.059	0.037	0.038	0.031	0.030	0.041	0.047	0.027	0.019
Nd	0.322	0.330	0.309	0.340	0.285	0.305	0.305	0.229	0.206	0.220	0.180	0.287	0.264	0.175	0.125
Pr	0.083	0.085	0.087	0.089	0.067	0.083	0.089	0.084	0.071	0.058	0.080	0.071	0.069	0.050	0.042
Ce	0.493	0.502	0.490	0.452	0.523	0.470	0.605	0.541	0.520	0.548	0.487	0.546	0.437	0.451	0.414
La	0.139	0.149	0.143	0.150	0.121	0.107	0.163	0.148	0.207	0.231	0.242	0.170	0.135	0.180	0.157
Y	0.016	0.011	0.023	0.025	0.016	0.026	0.040	0.023	0.057	0.043	0.135	0.037	0.079	0.133	0.129
Th	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.035	0.000
$\Sigma M^{(+3,+4)}$	1.166	1.194	1.152	1.141	1.111	1.091	1.299	1.097	1.102	1.153	1.208	1.152	1.031	1.093	0.899
$\Sigma(M^H, A^P)$	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Sum_Cat	12.012	11.995	11.939	11.972	11.969	12.014	12.016	11.990	11.825	12.002	11.841	11.903	12.027	12.069	11.871
F	2.865	2.832	3.012	2.985	2.944	2.905	2.713	2.901	2.988	2.759	2.571	2.836	2.877	2.799	3.204
O	15.135	15.168	14.988	15.015	15.056	15.095	15.287	15.099	15.012	15.241	15.429	15.164	15.123	15.201	14.796

Table 2. Representative trace-element LA-ICP-MS data (ppm) for nacacarenioibsite-(Ce) from the Papanduva peralkaline granite (sample MR-02). ID = crystal/spot identification. Deviations (2σ) are given in absolute values for a 95 % confidence level. Li, Cs, Sc, V, Cr and Ni, close or below the detection limit, were omitted, La, Ce and Pr not analyzed. b.d.: below detection limit.

Mineral	Nacacarenioibsite-(Ce)											
Point_ID	2.1		2.2		3.1		3.2		5.1		5.2	
	ppm	2σ	ppm	2σ	ppm	2σ	ppm	2σ	ppm	2σ	ppm	2σ
Li	8.7	0.9	9.6	0.9	b.d.		8.6	0.9	7.4	0.8	8.2	0.9
Sc	1.1	0.2	1.3	0.2	3.9	0.7	1.1	0.2	0.6	0.1	1.7	0.2
Mn	8.4	0.6	31.3	2.0	5.8	0.9	7.9	0.6	9.7	0.7	17.3	1.1
Co	0.27	0.06	0.20	0.06	0.30	0.22	0.28	0.06	0.18	0.07	1.77	0.15
Cu	0.40	0.09	0.61	0.11	4.29	0.78	0.41	0.09	0.26	0.09	0.27	0.09
Zn	85	5	91	6	90	7	90	6	75	5	83	5
Ga	38	2	40	2	80	5	38	2	32	2	33	2
Rb	0.9	0.1	1.1	0.1	0.9	0.2	0.7	0.1	1.4	0.1	3.5	0.2
Sr	635	39	637	39	756	50	655	40	624	39	666	41
Y	b.d.		b.d.		2258	145	b.d.		b.d.		b.d.	
Zr	18	1	49	3	256	19	29	2	10	1	52	4
Sn	3.4	0.4	2.9	0.4	6.4	1.4	2.9	0.4	2.0	0.4	3.1	0.4
Cs	1.21	0.09	1.16	0.08	1.12	0.15	1.12	0.08	1.1	0.1	3.2	0.2
Ba	249	15	253	15	191	12	250	15	196	12	209	13
Nd	52143	3192	56570	3467	50722	3187	60122	3691	43564	2661	46416	2835
Sm	8956	548	9525	583	11940	750	9828	602	9338	572	10133	621
Eu	257	16	277	17	277	18	284	17	271	17	274	17
Gd	5451	334	5348	328	6806	428	5711	350	5717	351	6039	371
Tb	617	38	681	42	617	39	681	42	697	43	697	43
Dy	2420	149	2695	166	1878	119	2703	167	2759	170	2610	161
Ho	296	18	342	21	177	11	334	21	361	22	332	21
Er	581	36	677	42	315	20	651	40	679	42	625	39
Tm	40	3	51	3	16	1	49	3	46	3	45	3
Yb	170	11	222	14	66	5	210	13	174	11	191	12
Lu	11.3	0.7	15.6	1.0	4.6	0.5	15.0	0.9	11.4	0.7	13.8	0.9
Hf	4.8	0.3	6.2	0.4	5.7	0.7	5.3	0.4	2.3	0.2	12.2	0.8
Ta	b.d.		b.d.		4183	269	b.d.		b.d.		56.6	3.6
Pb	13.1	0.8	14.0	0.9	8.1	0.9	15.3	1.0	22.4	1.4	26.3	1.7
Th	33.4	2.1	46.8	2.9	4.3	0.5	41.6	2.6	7.7	0.5	17.9	1.2
U	26.4	1.6	25.4	1.5	11.5	0.8	23.8	1.5	26.7	1.6	21.5	1.3

Table 3. Representative WDS compositions (wt. %) and structural formulae for britholite-(Ce). Structural formulae computed according to Oberti et al. (2001).
Point_ID: crystal/spot identification, c: core, r: rim, i: intermediate (our data, sample MR-03). Other analyses: A: Oberti et al. (2001), B: Kalsbeek et al. (1990), C: Orlandi et al. (1989), D: Arden & Halden (1999), E: Nash (1972). (*): mean analyses. b.d.: below detection limit, n.r.: not reported.

Mineral	Britholite-(Ce)														
Point_ID	1_i	2_i	1_c	2_c	2_i	2i	2_r	3_c	3_i	3_r	A	B*	C*	D*	E*
SiO ₂	19.39	19.46	19.77	20.29	20.01	20.23	20.13	19.94	19.95	19.50	21.10	17.10	20.89	19.56	16.20
ThO ₂	0.24	0.31	0.31	0.15	0.19	0.26	0.31	0.00	0.15	0.27	11.92	n.r.	20.73	1.12	n.r.
UO ₂	0.02	b.d.	b.d.	0.05	b.d.	b.d.	0.10	b.d.	b.d.	b.d.	2.12	n.r.	1.47	0.78	n.r.
Al ₂ O ₃	b.d.	0.02	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.02	b.d.	0.00	n.r.	n.r.	n.r.	0.09
La ₂ O ₃	15.28	13.95	15.76	16.70	16.49	17.79	16.96	17.32	16.70	14.90	11.23	17.98	7.35	8.67	16.30
Ce ₂ O ₃	32.15	32.62	32.64	32.02	33.87	31.56	31.89	31.80	31.23	33.77	21.70	29.42	18.61	25.48	22.50
Pr ₂ O ₃	3.75	4.14	3.17	3.78	3.58	3.60	3.88	2.98	3.44	3.65	2.19	2.48	1.64	n.r.	2.79
Nd ₂ O ₃	14.36	13.65	13.57	13.41	13.46	14.15	13.89	14.20	14.57	13.21	5.92	7.55	5.10	13.62	6.92
Sm ₂ O ₃	2.56	1.92	2.07	2.00	2.28	2.20	2.47	2.30	2.06	2.25	0.72	n.r.	n.r.	2.02	1.66
Gd ₂ O ₃	1.38	1.30	1.72	1.42	1.80	1.89	1.69	2.07	1.81	0.89	0.50	n.r.	n.r.	1.27	2.85
Dy ₂ O ₃	0.41	0.69	0.43	0.78	0.63	0.59	0.50	0.44	0.73	0.34	0.31	n.r.	n.r.	0.54	0.29
Yb ₂ O ₃	0.04	0.00	0.12	0.15	0.08	0.01	0.04	0.10	0.15	0.05	0.12	n.r.	n.r.	n.r.	0.18
Y ₂ O ₃	1.34	1.23	1.38	1.49	1.44	1.43	1.38	1.71	1.50	0.72	1.71	n.r.	n.r.	2.07	0.40
FeO	0.15	0.12	0.10	0.03	b.d.	0.05	0.08	b.d.	b.d.	0.13	0.00	n.r.	n.r.	n.r.	n.r.
MnO	0.05	0.11	0.06	0.02	0.08	0.05	0.14	0.15	0.10	0.22	0.00	n.r.	n.r.	n.r.	n.r.
MgO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.00	n.r.	n.r.	n.r.	0.02
CaO	3.58	4.39	3.74	3.28	3.34	3.27	3.33	3.50	3.22	4.61	16.80	11.93	19.92	14.56	16.60
BaO	0.15	0.04	0.04	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	0.10	0.00	0.00	n.r.	n.r.	n.r.
Na ₂ O	2.11	2.32	2.05	1.66	1.66	1.71	1.66	1.92	1.66	1.76	0.00	1.91	n.r.	n.r.	n.r.
P ₂ O ₅	1.09	2.01	1.28	0.16	0.20	0.12	0.20	0.20	0.07	1.18	1.11	8.07	4.30	2.94	7.03
F	1.90	2.14	2.04	1.69	1.45	1.51	1.73	2.20	1.75	2.39	2.12	0.00	n.r.	2.99	3.80
F=O	0.95	1.07	1.02	0.85	0.72	0.75	0.87	1.10	0.87	1.20	1.06	0.00	n.r.	1.49	1.90
Sum	99.00	99.36	99.23	98.23	99.84	99.67	99.52	99.81	98.24	98.74	98.51	96.44	100.01	94.10	95.73

Table 3. cont.

Structural formulae [26 (O,F) a.p.f.u.]

Point_ID	1_i	2_i	1_c	2_c	2_i	2i	2_r	3_c	3_i	3_r	A	B*	C*	D*	E*
Si	5.607	5.487	5.651	5.923	5.800	5.860	5.841	5.784	5.871	5.615	5.635	4.388	5.211	5.347	4.278
P	0.266	0.480	0.310	0.040	0.050	0.030	0.048	0.050	0.018	0.287	0.251	1.753	0.908	0.679	1.572
Sum_T	5.873	5.967	5.961	5.964	5.850	5.890	5.889	5.834	5.889	5.902	5.886	6.142	6.119	6.026	5.849
Th	0.016	0.020	0.020	0.010	0.013	0.017	0.020	0.000	0.010	0.018	0.724	0.000	1.177	0.070	0.000
U	0.001	0.000	0.000	0.003	0.000	0.000	0.007	0.000	0.000	0.000	0.126	0.000	0.082	0.047	0.000
Al	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.028
La	1.629	1.450	1.661	1.798	1.762	1.900	1.815	1.853	1.812	1.582	1.106	1.702	0.676	0.874	1.587
Ce	3.404	3.367	3.415	3.423	3.594	3.347	3.389	3.377	3.365	3.560	2.122	2.764	1.699	2.550	2.175
Pr	0.395	0.426	0.330	0.402	0.378	0.379	0.410	0.315	0.368	0.383	0.213	0.232	0.149	0.000	0.268
Nd	1.483	1.374	1.385	1.399	1.393	1.463	1.440	1.471	1.531	1.358	0.565	0.692	0.454	1.329	0.653
Sm	0.256	0.187	0.204	0.201	0.227	0.219	0.247	0.230	0.208	0.223	0.066	0.000	0.000	0.191	0.151
Gd	0.132	0.121	0.163	0.137	0.173	0.182	0.162	0.199	0.176	0.085	0.044	0.000	0.000	0.115	0.249
Dy	0.038	0.062	0.039	0.073	0.059	0.055	0.046	0.041	0.069	0.031	0.027	0.000	0.000	0.048	0.025
Yb	0.004	0.000	0.011	0.013	0.007	0.001	0.003	0.009	0.014	0.004	0.010	0.000	0.000	0.000	0.014
Y	0.206	0.184	0.211	0.232	0.222	0.220	0.213	0.264	0.236	0.111	0.243	0.000	0.000	0.302	0.056
Fe	0.037	0.029	0.023	0.008	0.000	0.012	0.020	0.000	0.000	0.032	0.000	0.000	0.000	0.000	0.000
Mn	0.012	0.027	0.015	0.004	0.018	0.011	0.034	0.036	0.025	0.055	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008
Ca	1.109	1.326	1.145	1.025	1.038	1.016	1.036	1.087	1.016	1.423	4.807	3.280	5.324	4.264	4.696
Ba	0.017	0.005	0.004	0.000	0.000	0.000	0.000	0.006	0.000	0.011	0.000	0.000	0.000	0.000	0.000
Na	1.183	1.268	1.137	0.940	0.933	0.961	0.933	1.080	0.947	0.982	0.000	0.950	0.000	0.000	0.000
Sum_REE	9.921	9.851	9.762	9.670	9.819	9.785	9.775	9.969	9.783	9.857	10.054	9.620	9.561	9.788	9.912
F	1.741	1.911	1.840	1.563	1.325	1.381	1.588	2.021	1.624	2.180	1.791	0.000	0.000	2.581	3.173

Table 4. Representative LA-ICP-MS trace-element abundances for britholite-(Ce) from the Papanduva peralkaline granite (sample MR-03). ID = crystal/spot identification. Deviations (2σ) are given in absolute values for a 95 % confidence level. Li, Cs, Sc, Ti, Cr, Co, Ni, and Cu, with abundances close or below the detection limit, were omitted, La, Ce, Pr and Nd, not analyzed.

Mineral	Britholite-(Ce)											
Point_ID	1.1.		1.2		2.1		2.2		1.3		2.3	
Element	ppm	2σ	ppm	2σ	ppm	2σ	ppm	2σ	ppm	2σ	ppm	2σ
Be	b.d.		b.d.		b.d.		b.d.		1.4	1.1	b.d.	
Mg	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Sc	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Mn	354	37	413	43	399	42	433	46	286	58	322	65
Ga	81	10	82	10	85	10	95	12	86	6	94	6
Rb	b.d.		1.0	0.2	0.5	0.3	1.1	0.3	0.8	0.2	0.6	0.1
Sr	1208	683	1628	920	1221	691	1139	644	3379	7859	3192	7425
Y	1502	110	b.d.		b.d.		b.d.		200	41	b.d.	
Zr	b.d.		b.d.		0.8	0.4	0.5	0.4	b.d.		b.d.	
Nb	8	1	15	2	16	2	18	2	11	1	12	1
Sn	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Ba	602	57	615	59	640	61	692	66	471	80	473	81
Sm	9477	1141	11441	1378	11853	1431	12181	1472	7741	489	8676	551
Eu	260	24	330	30	322	30	329	30	222	37	269	44
Gd	5326	346	7708	500	8765	574	8593	565	4281	502	5794	680
Tb	546	36	801	53	786	53	768	52	491	33	609	42
Dy	2372	247	3736	389	3272	342	3250	340	2409	194	2204	178
Ho	286	28	469	47	408	41	393	39	379	40	331	35
Er	522	34	871	56	724	47	717	47	710	78	571	63
Tm	41	4	73	6	58	5	58	5	56	4	51	3
Yb	168	18	293	30	249	26	244	26	238	20	219	19
Lu	12.2	1.0	22.2	1.8	19.7	1.6	19.1	1.6	16.5	1.1	15.8	1.1
Hf	b.d.		b.d.		b.d.		0.2	0.1	0.3	0.1	0.2	0.1
Ta	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Pb	1714	213	1858	230	1849	230	2032	253	1184	160	1409	190
Th	1020	67	1531	101	1170	78	1297	87	965	75	873	68
U	67	8	82	9	59	7	61	7	66	13	46	9

5.1. NACARENIBOSITE-(Ce)

Representative chemical data for nacareniosite-Ce, rinkite and “mosandrite” are listed in Table 1. Nacareniosite-(Ce) from the Morro Redondo Complex is relatively homogeneous, and compared to literature data is the one that most closely approaches the end-member composition with $10.7 \leq \text{Na}_2\text{O} \leq 11.1$ wt. % (2.67 - 3.06 a.p.f.u.) and $14.8 \leq \text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5 \leq 15.8$ wt. % (0.93 - 0.99 a.p.f.u.). The calculated, mean formula based on 16 analyses is $\text{Na}_{3.0}(\text{Ca}_{2.75}\text{Sr}_{0.01})_{2.76}(\text{REE}, \text{Y})_{1.16}(\text{Nb}_{0.95}\text{Ta}_{0.02}\text{Ti}_{0.04})_{1.01}\text{Si}_{3.99}\text{O}_{14}(\text{O}_{1.11}\text{F}_{2.89})_4$. In general, the lathy crystals

that form the fibrous aggregates contain somewhat higher TiO₂ and lower Nb₂O₅ and Ta₂O₅ abundances.

Based on ideal formulae and available data, Petersen et al. (1989) suggested the existence of an extensive solid solution series between the end members rinkite, with the ideal formula Na₂Ca₄(REE)Ti (Si₂O₇)₂OF₃, and nacareniobsite-(Ce), related by the [Ti⁺⁴Ca²⁺]₋₁[Nb⁵⁺Na⁺] coupled exchange substitution. The authors also indicate that the observed compositional variations among the rinkite-related minerals, such as rinkolite and götzenite, follow the [Ca²⁺]₋₂[REE³⁺Na⁺] substitution. Recently, Cámara et al. (2011) show that the available rinkite and nacarebiosite-(Ce) compositions lie on a plane within the (Nb, REE+Y, Na) space, which is defined by the equation Na = 1.34 + 0.81*Nb + 0.67*(REE,Y). Of interest, the mineral name 'rinkite' was to be eliminated given the precedence of the name mosandrite (e.g., Fleischer, 1958). However, the structure of the mosandrite holotype was not determined, and Sokolova and Cámara (2008) indicate that the chemical composition and structural topology of mosandrite (type locality) and rinkite (Galli & Alberti, 1971) are identical. Thus, Cámara et al. (2011) concluded that mosandrite requires redefinition. Accordingly, the mineral name rinkite will be adopted in the subsequent sections.

The main compositional variations for representative rinkite and nacareniobsite-(Ce) compositional data are shown in Figs. 3A and 3B. Below, the main exchange reactions of Petersen et al. (1989) have been slightly modified to accommodate some minor substitutions of Ca, Nb and Ti for other measurable cations with equivalent charges and site preferences:

and

in which equation (1) involves the A^P, M^O_(2,3) and M^H and equation (2) the A^P, M^O₍₁₎ and M^H cation sites in the structural scheme defined by Sokolova & Hawthorne (2008). A compilation of the existing literature data reveals poor oxide totals and/or inappropriate structural formulae and hence

such analyses were not considered in Figure 3. The ideal rinkite and nacareniobsite-(Ce) end-members are also shown in Fig. 3A.

Figure 3. Representative compositions of rinkite, in green, and nacareniobsite-(Ce), in blue and black, in the cationic diagrams A: $M^{2+} + M^{4+}$ vs. $Na + M^{5+}$ and B: $2M^{2+}$ vs. $Na + (REE, Y)$. The ideal rinkite and nacareniobsite-(Ce) end-members are plotted in red. Note the exceptional correlation of the available data in both diagrams. Symbols: open triangles: “mosandrite” from the type locality (Sokolova & Cámara, 2008), full triangles: Cámara et al. (2011), open diamonds: Petersen et al. (1989), filled diamonds (Sokolova & Hawthorne, 2008), crosses: Ridolfi et al. (2006), open circles: this work. See discussion in the text.

As depicted in Fig. 3A, the data align very well along the join between the ideal rinkite and nacareniobsite-(Ce) end-members and give an exceptional determination coefficient $r^2 = 0.99$. This diagram clearly demonstrates an almost complete solid solution series between these two minerals, as previously suggested by Petersen et al. (1989). The “mosandrite” from the type locality and in particular the nacareniobsite-(Ce) from the Morro Redondo Complex compositions plot very close to the ideal end-members. Their molecular compositions may therefore be defined by $rnk_{91.6} ncr_{8.4}$ and $rnk_{04} ncr_{96}$, respectively given the $(Nb+Ta)/(Ti+Zr)$ relationships in the $M^{O}_{(1)}$ site, where rnk = rinkite and ncr = nacareniobsite. In detail, a minor shift from the end-members join towards relatively lower bivalent and tetravalent cation totals, which is more evident in the nacareniobsite-(Ce) analyses, is

inferred from Fig. 2. Thus, the significance of reaction (2) augments as the Na/Ca and/or Nb/Ti ratios increase in the crystallization environment (Fig. 3B), and hence imply higher relative occupancies of REE+Y into the mineral structure (cf. next section), certainly in excess of 1 a.p.f.u. This could explain why some of the data reported here possibly include some minor Na excess relative to the ideal 3.0 a.p.f.u. of the $M^{O}_{(2)}$ and the two equivalent $M^{O}_{(3)}$ sites. If this is correct, then the excess Na must fill in the M^H sites (cf. Table 2).

5.1.1. REE and trace-element patterns

REE+Y contents in nacareniobsite-(Ce) investigated here vary between 21.1 and 24.9 wt. % (1.08 – 1.28 a.p.f.u.) and are in general higher than literature data (cf. Table 1). REE+Y chondrite normalized patterns are displayed in Figure 4, and compared to literature data the REE+Y contents reported here are between 4 and 5 time higher. In Fig. 4A, patterns for nacareniobsite-(Ce) and rinkite obtained here are homogeneous and display a concave LREE region, and are compared to literature data for rinkite and “mosandrite”. Complete REE chondrite-normalized patterns are shown in Fig. 4B and these display steep, negatively sloped lines. A well-developed negative Eu anomaly is typical, with $Eu^* [= Eu/(Sm \cdot Gd)^{0.5}]$ between 0.09 and 0.13.

Expanded host-rock normalized trace element patterns are depicted in Fig. 5. Relative to the host granite, nacareniobsite-(Ce) is enriched in LREEs, MREEs, Sr and Y (up to 2.9, in orders of magnitude), and depleted in alkali metals, in particular Rb, and Zr. The abundances of the remaining elements are similar, with relative enrichment or depletion (compared to the host granite) within 1.5 orders of magnitude.

Figure 4. Representative rinkite and nacaraeniosite-(Ce) REE patterns. A: partial EPMA data, symbols as in Fig. 3, to which data from Nagy (2003), left-full triangles, and Pekov & Ekimenkova (2001), right-full triangles, were added. B: complete combined EPMA-LA-ICP-MS patterns for nacaraeniosite-(Ce) from the Papanduva peralkaline granite (sample MR-02). Normalizing factors after Boynton (1984). See discussion in the text.

5.1.2. Unidentified Nb-rich phase

As stated above, the nacaraeniosite-(Ce) crystals investigated here contain minute internal areas that were problematical for WDS analyses, with higher BSE compositional signals (Fig. 3C), corresponding to unidentified Nb-rich phases. Compared to EDS patterns for nacaraeniosite-(Ce), those for the unidentified phases contain higher Nb (up to 2-fold) and lower Si (up to 0.5-fold), Ca (0.5-fold) and REEs, and similar Na uncorrected intensities. The chemical nature of these areas (with the exception of their relative elemental intensities) are very similar to those described by Petersen et al. (1989) for nacaraeniosite-Ce from the Ilímaussaq Complex and attributed to Na- and Ca-leaching due to alteration processes. However, in our case, these areas are not depleted in Na to a significant extent nor significantly enriched in the REEs, differences that certainly must be related to contrasted late-fluids compositions involved in each case.

Figure 5. Representative multi-element patterns for nacareniobsite-(Ce) from the Papanduva peralkaline granite, as normalized to the host rock (sample MR-02).

5.2. BRITHOLITE-(Ce)

Britholite-(Ce) and REE-fluorcarbonate bastnesite, which occurs as a substitution product in the studied samples and also as independent crystals in other samples (e.g., Vilalva, 2007), are the (REE,Y)-richest minerals in the peralkaline granites from the Morro Redondo Complex. The britholite-(Ce) is classified as britholite *senso strictu*, with $\Sigma(\text{REE,Y}) > \text{Ca}$ (Pekov et al., 2007) and their (REE,Y) contents are among the highest reported to date with up to 73.6 wt. % oxide (9.98 a.p.f.u.). SiO_2 and Na_2O abundances are also relatively higher, whereas the P_2O_5 and CaO contents are lower. The total variation of the F contents is 1.45 - 2.63 wt. % and some of these in addition to the literature data (cf. analyses 3_r, D* and E* in Table 3) may in fact represent fluorbritholite (Gu et al., 1994). Of note, the structural formulae computed on the basis of 26 (O,F) indicate a minor systematic deficit in the tetrahedral sites with $\text{ca. } 5.80 \leq (\text{Si} + \text{P}) \leq 5.97$ a.p.f.u. (cf. Table 3). On the basis of the study by Oberti et al. (2001), such deficiencies may be indicative of unanalyzed B filling in these structural positions.

The main compositional variations observed in the britholite series are analogous to those observed in the apatite group, and may be attributed to the $[\text{PM}^{2+}]_{-1}[\text{Si}(\text{REE},\text{Y})]$ and $[\text{M}^{2+}]_2[\text{Na}(\text{REE},\text{Y})]$ coupled substitution mechanisms (e.g., Rønsbo, 1989; Kalsbeek et al., 1990; Fleet & Pan, 1995; Chang et al., 1998; Oberti et al., 2001; Pan & Fleet, 2002; Chen & Simonetti, 2012). The compositions reported here and those compiled from the literature are evaluated on the basis of these substitution schemes (Fig. 6). The trends shown in Figure 6 clearly demonstrate the effectiveness of both mechanisms since these define high determination coefficients ($r^2 = 0.97$). As expected, the compositional data obtained here plot in the areas with the highest $[\text{Si} + (\text{REE},\text{Y})]$ - and $[\text{Na} + (\text{REE},\text{Y})]$ contents. Importantly, the EPMA data also reveals a relatively good positive correlation between P and F contents (not shown), which suggests a more general substitution mechanism for the first scheme to include $[\text{OH}]_{-1}\text{F}$, such as:

Th and U are not significant constituents in the britholite-(Ce) investigated here, however ThO_2 and/or UO_2 contents for literature data are very high, up to 20.7 and 1.5 wt. % (cf. analysis A* and C*), respectively. The incorporation of both elements in the britholite-(Ce) and apatite structures may be attributed (amongst others) by the $[\text{M}^{2+}(\text{REE},\text{Y})]_{-1}[\text{Na}(\text{Th},\text{U})]$ and $[\text{M}^{2+}(\text{Th},\text{U})]_{-1}[(\text{REE},\text{Y})]_2$ coupled substitution schemes (see Pan & Fleet, 2002). The britholite-(Ce) data reported here suggest that the second substitution mechanism (listed above) is the most important in britholite-(Ce) (Fig. 7).

Figure 6. Representative compositions of britholite-(Ce) in the cation diagrams A: $P + M^{2+}$ vs. $Si + (REE, Y)$ and B: $2M^{2+}$ vs. $Na + (REE, Y)$. Note the high correlation defined by the data in both diagrams. Symbols in red: triangles up, Kalsbeek et al. (1990); diamonds, Oberti et al. (2001); crosses, Orlandi et al. (1989), triangle down, Arden & Halden (1999); square, Nash (1972); black open circles, this work. See discussion in the text.

Figure 7. Representative compositions of britholite-(Ce) in the cation diagram $M^{2+} + (Th, U)$ vs. $2(REE, Y)$, which display a high degree of correlation. Symbols as in Fig. 6.

5.2.1. REE and trace-element patterns

Chondrite-normalized REE and expanded trace element host-rock normalized patterns for britholite-(Ce) are displayed in Figs. 8 and 9; Fig. 8A also displays representative literature data for britholite. With the exception of two samples from previous studies that contain higher La and similar Ce contents, the analyses reported here are overall more enriched in the remaining REEs and define ‘smooth’ negatively sloped patterns (Fig. 8B). As with nacareniobsite-(Ce), britholite-(Ce) is characterized by a significant negative Eu anomaly with $0.06 \leq \text{Eu}^* \leq 0.24$. The data reported here suggest two compositional groups, in particular based on the Dy and Y contents (Fig. 8A). In general, the Y-rich compositions are typically observed in crystal cores or intermediate zones, and therefore it may be concluded that britholite-(Ce) evolved to relatively (HREE, Y)-poor compositions as crystallization proceeded. Relative to the host granite, britholite-Ce is significantly enriched in the L-MREEs and Sr, marked by depletions in Rb, Zr and Hf, and minor enrichments in Ba, Th, U and Pb, up to 1.3 orders of magnitude (Fig. 9).

Figure 8. Representative britholite-(Ce) REE patterns, normalized after Boynton (1984). A: partial EPMA data, symbols as in Fig. 6. B: complete combined EPMA-LA-ICP-MS patterns for britholite-(Ce) from the Papanduva peralkaline granite (sample MR-03). Normalizing factors after Boynton (1984). See discussion in the text.

Phosphate minerals, in particular monazite and xenotime, may be considered excellent U-Th-Pb chronometers (e.g., Harrison et al., 2002). Of interest, the measured Pb contents in the britholite-(Ce) analyses reported here exceed the expected abundances generated by Th and U radioactive decay (given its Neoproterozoic age), thus implying that britholite-(Ce) contains a significant amount of common Pb.

Figure 9. Representative multi-element patterns for britholite-(Ce) from the Papanduva peralkaline granite, as normalized to the host rock (sample MR-03).

6. CONCLUDING STATMENTS

6.1. CRYSTALLIZATION ENVIRONMENT

As with other plutons from the alkaline and aluminous petrographic association of the Graciosa A-type Province (e.g., Gualda & Vlach, 2007, Vlach and Gualda, 2007, Vilalva & Vlach, submitted), the emplacement of the peralkaline granites of the Papanduva Pluton occurred at relatively low crustal levels at pressures < 2kbar. The temperature ranges of crystallization for the peralkaline melts are difficult to assess, as pertinent mineral assemblages are lacking and the zircon saturation geothermometer does not apply to peralkaline systems (e.g. Watson & Harrison, 1983; Miller et al., 2003). Temperature estimates based on Ti-in-quartz geothermometry (Ward & Watson,

2006) should approach liquidus temperatures, as quartz was a relatively early crystallizing phase in high-Si peralkaline systems; this is also in agreement with their agpaitic crystallization sequence. Assuming $P = 1$ kbar and an a_{TiO_2} of 0.7, preliminary estimates yield a temperature range between 650° and 800°C for related peralkaline samples with low-deformed quartz crystals from related peralkaline samples. Nacareniobsite-(Ce)- and britholite-(Ce)-bearing granites containing recrystallized quartz within a granoblastic matrix yield much lower calculated temperatures of 400°C. In addition, the presence of ferrichterite suggests an upper temperature stability limit of 760°C in reduced (~WM buffer) conditions, and lower temperature stability of 535°C under QFM crystallization conditions (e.g., Charles, 1975); moreover, the presence of late-stage Na-amphibole suggests a magmatic temperature range between 800°C (liquidus) and ca.530°C (solidus; see also Ernst, 1968; Stolz, 1986; Marks et al., 2003; Pe-Piper, 2007).

The textural features indicate that a majority of the britholite-(Ce) was formed after close-to-solidus deformation episodes, as most crystals appear systematically broken. In relation to the nacareniobsite-(Ce), evidences are less straightforward but suggest a similar formational history. Considering the uncertainties of the above temperature estimates and some independent inferences obtained from peralkaline systems elsewhere (e.g., Marks et al., 2003; Macdonald, 2012), it is believed that both minerals may have formed at temperatures ~600°C or less.

The observed mineral parageneses in the peralkaline Papanduva granites point to initial melt crystallization under relatively reduced f_{O_2} conditions. The aenigmatite-bearing, magnetite- and ilmenite-absent main peralkaline granite (unit C of Vilalva and Vlach, 2010) formed within the 'no-oxide' field of Nicholls and Carmichael (1969), close to the fayalite-quartz-magnetite (FQM) buffer, or below in the case of the richterite-bearing samples. Typically, these melts evolved under an oxidizing conditions as indicated by, among other evidences, the occurrence of late-stage aegirine mantling Na- and Na-Ca-amphiboles (cf. details in Vilalva & Vlach, submitted). The post-magmatic crystallization stage was characterized by more oxidizing conditions at the magnetite-hematite (HM) buffer. The late stage of the complex's evolution was characterized by intense, deformation driven, circulation of residual melts and/or fluids, which precipitated most of the rare mineral assemblages

observed in the peralkaline granites. Preliminary high $\delta^{18}\text{O}$ values (e.g., 9.2 to 10.2 and 6.1 to 9.1 ‰ in quartz and K-feldspar, respectively) suggest no significant contributions from meteoritic waters *sensu strictu* to the magmatic system (e.g., Vilalva et al., submitted).

6.2. HOST-ROCK CONSTRAINTS ON MINERAL COMPOSITIONS

The occurrence of nacareniobsite-(Ce) in ‘supersaturated’ rocks, such as the peralkaline granites investigated here demonstrates that its stability, and arguably that of rinkite, does not depend much on the level of Si-saturation of the original melts. It is more probably related to the elements and co-precipitating mineral phases present in a F-rich, moderately-to-strong peralkaline crystallizing environment. As typically reported in peralkaline systems elsewhere (e.g., Marks et al., 2003; Marks et al., 2011; Schilling et al., 2011; Vlach and Gualda, 2007), both whole rock and mineral geochemistry indicate that melt peralkalinity increases as crystallization proceeds. In the subsequent late-magmatic stages, the relative peralkalinity increases, and importantly the Nb/Ti ratios correlate positively with the Agpaitic Index for the Papanduva Pluton (Vilalva and Vlach, submitted). Compared to nacareniobsite-(Ce) reported from other occurrences of saturated felsic rocks, the most remarkable compositional feature of the nacareniobsite-(Ce) described here is its higher Nb, Ta, (REE,Y) and, to a some extent, Na contents. This is clearly related to the chemical signature of the initial melts.

Whether the Papanduva peralkaline late-stage granites represent primary liquids or the product of crystal fractionation processes, these melts are significantly enriched in Na, HFSE, and F but contain lower Ca/Na ratios. These features along with their relatively high Nb/Ti ratios drive reactions (1) and (2) to the their extreme left side and yield compositions very close to the ideal nacareniobsite-(Ce) end-member. Similar factors have also constrained the britholite-(Ce) compositions, which are characterized by higher contents of Si, Na and (REE, Y) compared to most of those previously reported.

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ANEXO:

E

Major- and trace-element composition of *REE*-rich turkestanite from peralkaline granites of the Morro Redondo Complex, Graciosa Province, south Brazil

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ABSTRACT

Turkestanite, a rare Th- and *REE*-bearing cyclosilicate in the ekanite–steacyite group was found in evolved peralkaline granites from the Morro Redondo Complex, south Brazil. It occurs with quartz, alkali feldspar and an unnamed Y-bearing silicate. Electron microprobe analysis indicates relatively homogeneous compositions with maximum ThO₂, Na₂O and K₂O contents of 22.4%, 2.93% and 3.15 wt.%, respectively, and significant *REE*₂O₃ abundances (5.21 to 11.04 wt.%). The *REE* patterns show enrichment of *LREE* over *HREE*, a strong negative Eu anomaly and positive Ce anomaly, the latter in the most transformed crystals. Laser ablation inductively coupled plasma mass spectrometry trace element patterns display considerable depletions in Nb, Zr, Hf, Ti and Li relative to whole-rock sample compositions. Observed compositional variations suggest the influence of coupled substitution mechanisms involving steacyite, a Na-dominant analogue of turkestanite, iraqite, a *REE*-bearing end-member in the ekanite–steacyite group, ekanite and some theoretical end-members. Turkestanite crystals were interpreted as having precipitated during post-magmatic stages in the presence of residual HFSE-rich fluids carrying Ca, the circulation of which was enhanced by deformational events.

KEYWORDS: turkestanite, chemical composition, trace elements, solid solution, peralkaline granite, Graciosa Province, Brazil

Introduction

TURKESTANITE, first described by Ginzburg *et al.* (1965) under the name “Th–Ca–K silicate” in the Central Asia region, is a hydrous cyclosilicate in the ekanite–steacyite group of minerals. The group may be represented by the general formula $AB_2C[\text{Si}_8\text{O}_{20}]$, where $A = \text{Th, U, REE, Pb, Fe}^{3+}$; $B = \text{Ca, Na, REE}$ and $C = \text{K, Na, } \square$, where $\square =$ vacancy (Perrault and Szymański, 1982; Uvarova *et al.*, 2004) and comprises three known end-members: ekanite $\text{ThCa}_2[\text{Si}_8\text{O}_{20}]$, with *I*422 symmetry, as a distinct mineral species, and

steacyite $\text{Th}(\text{Na,Ca})_2\text{K}_{1-x}\square_x[\text{Si}_8\text{O}_{20}]$ and iraqite $\text{REE}(\text{Ca,Na})_2\text{K}_{1-x}\square_x[\text{Si}_8\text{O}_{20}]$, which may constitute an isomorphous series with *P4/mcc* symmetry (Agakhanov *et al.*, 2004). It is worth taking into consideration that several other theoretical end-members satisfy this formula: “*a*” $\text{REE}(\text{REE,Ca})\square[\text{Si}_8\text{O}_{20}]$, “*b*” $\text{Th}(\text{REE,Na})\square[\text{Si}_8\text{O}_{20}]$ and “*c*” $\text{REE}(\text{REE,Na})\text{K}[\text{Si}_8\text{O}_{20}]$, as well as U–Ca–K equivalents. Most steacyite and iraqite analyses reveal significant yet variable (~2.0–4.0 wt.%) water abundances (Perrault and Szymański, 1982; Livingstone *et al.*, 1976), but its role is rather uncertain. Available structural data suggest that it is a kind of “zeolitic”, exchangeable water (e.g. Petersen *et al.*, 1999).

Perrault and Szymański (1982) re-evaluated the nomenclature of ‘ekanite’-group minerals and

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suggested that the “Th-Ca-K silicate” represents a new mineral species. It was officially recognized as turkestanite after detailed studies by Pautov *et al.* (1997), with the crystal structure defined by Kabalov *et al.* (1998). These studies found the $P4/mcc$ symmetry and the ideal formula $(Th,REE)(Ca,Na)_2K_{1-x}\square_x[Si_8O_{20}].nH_2O$, where $x \approx 0.47$. Arapovite is a U^{4+} analogue of turkestanite with the ideal formula $(U,Th)(Ca,Na)_2K_{1-x}\square_x[Si_8O_{20}].H_2O$ (Agakhanov *et al.*, 2004). According to the authors, there is a continual isomorphous series between arapovite and turkestanite, and the presence of an isomorphous series between arapovite, steacyite and iraqite is possible, although intermediate phases in these series have yet to be reported.

Turkestanite is a very rare mineral and has been reported from only three other occurrences. Prismatic crystals were described in metasomatic zones in the outer portions of the Dzhelisu Massif (Kyrgystan) and Dara-i-Pioz (Tadjikistan) Alkaline Complex, associated with aegirine, hedenbergite, albite, microcline, fluorapatite and quartz (Pautov *et al.*, 1997; Reguir and Chakhmouradian, 1999), and as sparse crystals in small alkaline veins in the contact zone of the Ilimaussaq Complex (Greenland) associated with albite, microcline, aegirine, quartz, narsarsukite and eudialyte (Petersen *et al.*, 1999).

In this paper, we present textural and compositional EPMA and LA-ICP-MS data for turkestanite in peralkaline granites from the Papanduva Pluton, Morro Redondo Complex, located in the Graciosa Province of A-type granites and syenites, south Brazil (Gualda and Vlach, 2007). These peralkaline granites present a variety of late- to post-magmatic rare HFSE-bearing accessory minerals (e.g. Vilalva and Vlach, 2006; Vilalva, 2007), including the first-known occurrence of an ekanite–steacyite-group mineral in South America. We discuss compositional variations in turkestanite and identify new substitutions and solid solution ranges.

Geological and petrographic background

The Graciosa Province of A-type granites and syenites (Vlach *et al.*, 2006; Gualda and Vlach, 2007, Fig. 1) formed at ~580 Ma during extensional tectonics related to the Gondwana amalgamation in SE Brazil. It consists of several granitic and syenitic plutons emplaced at shallow crustal levels in Archaean and Neoproterozoic country rocks, with minor occurrences of volcanic

and dioritic rocks, which crop out mainly along the Serra do Mar Escarpment. The intrusive rocks are divided into two main petrographic associations (Gualda and Vlach, 2007; Vlach and Gualda, 2007): (1) an aluminous, ‘subalkaline’ association made up of subsolvus, metaluminous to weakly peraluminous, biotite granites, and (2) an alkaline association consisting of hypersolvus, metaluminous alkali-feldspar syenites and peralkaline alkali-feldspar granites.

The Morro Redondo Complex covers an area of ~250 km² and is one of the most important occurrences of the province. The complex consists of two distinct plutons: (1) the larger Quiriri Pluton, made up of weakly peraluminous biotite syenogranites; and (2) the Papanduva Pluton, composed of peralkaline alkali-feldspar granites. Minor rhyolites, basalts and andesitic basalts constitute a coeval bimodal volcanism. Previous work concerning the geology, petrography and geochemistry of these plutons has been presented by Machado *et al.* (1993), Vilalva and Vlach (2006), Vilalva (2007) and Vlach and Gualda (2007).

The Papanduva Pluton, as the northern portion of the Morro Redondo Complex (Fig. 1), is made up of medium- to fine-grained, leucocratic to hololeucocratic (colour index between 2 and 8) alkali-feldspar granites, consisting essentially of mesoperthitic alkali feldspar, quartz and interstitial aegirine and/or sodic or sodic-calcic amphiboles as the main mafic phases. Zircon, astrophyllite, fluorite, chevkinite, aenigmatite and ilmenite are the most common primary accessory minerals. These granites are among the most evolved peralkaline rocks in the Graciosa Province, with an agpaite index $[(Na_2O+K_2O)/Al_2O_3]_{mol}$ between 1.02 and 1.13 (Vlach and Gualda, 2007).

Four distinct units, named A, B, C and D, were mapped on the basis of mineralogical, textural and/or structural criteria (Vilalva, 2007). Unit A is unique in its unusual late- to post-magmatic mineralogical content. It presents an oriented structure and late-magmatic to solid-state deformation-type textures, marked by alkali feldspar and arfvedsonite porphyroclasts (2.0–4.0 mm long), the latter sometimes with post-magmatic aegirine mantles, in a granoblastic fine-grained matrix with quartz, microcline, albite and aegirine. Accessory late- to post-magmatic minerals include narsarsukite, britholite, nacareniobite, neptunite, (Na-K) zirconosilicates, turkestanite, and some as-yet unidentified phases (Vilalva and Vlach, 2006; Vlach and Vilalva, 2007).

FIG. 1. Geological sketch map showing the Neoproterozoic, A-type Graciosa Province in southern Brazil (dark grey plutons) and the Morro Redondo Complex (1) with the Papanduva Pluton highlighted (light grey). The black star is the approximate location of the turkestanite-bearing samples studied. The main regional tectonic units are: A – Ribeira Fold Belt, B – Curitiba Domain, C – Luiz Alves Craton and D – Paranaguá Domain (Coastal Granitoid Belt). Adapted from Prazeres Filho *et al.* (2003) and Gualda and Vlach (2007).

Analytical methods

Compositional data for turkestanite were obtained using electron probe microanalysis (EPMA, WDS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Departamento de Mineralogia e Geotectônica do Instituto de Geociências da Universidade de São Paulo, Brazil. The WDS microanalyses were performed on C-coated polished thin sections using a JEOL JXA8600S instrument, under analytical conditions of 15 kV, 20 nA and 10 μ m, respectively, for the column accelerating voltage, beam current and diameter. We have tested the susceptibility of the Morro Redondo turkestanite under various beam conditions examining the variation of gross peak counts *vs.* time for the most relevant elements analysed and observed that, under such conditions, the mineral remains stable. Backscattered electron (BSE) images were used to identify qualitatively the zonation within the grains in order to guide the location of quantitative analyses. The elements

analysed, spectral lines, background offsets, total integration times and standards used in the analytical routine are listed in Table 1. We used natural and synthetic standards, including the REE phosphates of Jarosewich and Boatner (1991). Matrix corrections of the raw intensity data were made using the PROZA procedure (Bastin and Heijligers, 1990). The overlap of Th on U $M\alpha$ line intensities was corrected with the program *Age_Cor* (cf. Vlach, 2010). Estimated precision is better than 2% for major elements, between 5 and 10% for minor elements, and higher for traces.

The EPMA analyses of minerals with significant quantities of H₂O must account for the O included in H₂O molecule for appropriate matrix corrections, especially for light elements. Thus, we fixed a somewhat arbitrary H₂O mean value at 5.35 wt.%, based on what is missing, to make up 100.0 wt.% in our analyses. This value, although greater than that verified in other turkestanite analyses in the literature (~0.3–1.8 wt.%; Pautov

TABLE 1. Analytical conditions used for turkestanite electron microprobe (WDS) analysis. Total counting time equally divided into peak and background.

Element	Spectral line	Diffracting crystal (spectrometer)	Background offsets (mm)		Total integration time (s)	Standard
			(-)	(+)		
Si	<i>Kα</i>	PET (2)	0.90	0.90	5	BaAl ₂ Si ₂ O ₈
Th	<i>Mα</i>	PET (2)	1.60	1.60	10	ThSiO ₄
U	<i>Mα</i>	PET (3)	1.80	1.55	30	UO ₂
Al	<i>Kα</i>	TAP (1)	3.25	0.85	30	YAG
La	<i>Lα</i>	LiF (5)	1.45	1.65	10	LaPO ₄
Ce	<i>Lα</i>	LiF (5)	1.45	1.65	10	CePO ₄
Pr	<i>Lβ</i>	LiF (5)	0.75	0.85	10	PrPO ₄
Nd	<i>Lβ</i>	LiF (5)	0.90	1.00	10	NdPO ₄
Sm	<i>Lβ</i>	LiF (5)	0.55	0.55	20	SmPO ₄
Gd	<i>Lβ</i>	LiF (5)	1.00	1.00	20	GdPO ₄
Y	<i>Lα</i>	PET (2)	1.95	0.70	20	YAG
Fe	<i>Kα</i>	LiF (5)	0.75	0.65	10	Olivine ^N
Ca	<i>Kα</i>	LiF (5)	0.70	1.10	10	Ca ₂ P ₂ O ₇
Pb	<i>Mα</i>	PET (4)	3.65	3.90	50	PbCr ₂ O ₄
Na	<i>Kα</i>	TAP (1)	0.55	0.45	5	Amelia albite ^N
K	<i>Kα</i>	PET (3)	1.25	1.20	10	Asbesto microcline ^N

^N: natural standard

et al., 1997) is possible, once the water in the ekanite–steacyite-group minerals are exchangeable, as mentioned, and weight losses on heating above 10% at 700–800°C have been reported (Perrault and Richard, 1973).

Laser ablation analyses were carried out in raster mode (continuous ablation trench) for a single turkestanite crystal in a 30 µm thick thin section using the Elan 6100DRC ICP-MS equipped with a New Wave UP-213 laser ablation system, with a 213 nm Nd-doped YAG laser. The laser beam diameter at the sample surface was 45 µm. The total acquisition time used was 120 s, equally divided for blank and sample measurements. Forty four elements were analysed, with signal integration time and dwell time of 8.3 and 1.66 ms respectively. Data acquisition, drift corrections, as well as final data treatment and conversions to concentration were achieved using the *Glitter* software (Van Achterbergh *et al.*, 1999). Synthetic glasses SRM-612 (NIST) and BHVO-2G were used as standards. The average abundances of Si and Ca obtained from the EPMA were used to normalize their measured intensities.

Mineral formulae and cationic distribution were obtained using the program *Mincal* (Gualda and Vlach, unpublished), based on the

sum of tetravalent cations (Si + Al) = 8.0, taking all Fe as Fe³⁺, according to Pautov *et al.* (1997).

Results

Textural and optical characteristics

Three turkestanite-bearing granite samples (MR-02A, MR-02(2) and MR-140, cf. Fig. 1) from the Papanduva Pluton were studied in this work. In these samples, turkestanite crystals are pale-yellow/pale-brown subhedral/euhedral prisms, 0.3–0.5 mm long, with a basal parting; basal sections are roughly four-sided. Birefringence is 0.004–0.005 and it is optically negative. Turkestanite occurs in close association with an unnamed isotropic (Y-*HREE*)-bearing hydrated silicate, filling in interstices among quartz, microcline and albite.

All the crystals analysed show roughly concentric zoning in optical and/or BSE images. In general, crystal cores are more transparent and pristine than the rims, which have a turbid aspect, a dark-brown color, and are more micro-fractured (Figs 2a, 3a), but the converse sometimes occurs (Fig. 2b). Crystals from the MR-02(2) sample show complex convolute zoning defined by contrasting turbid darker, and transparent lighter domains

FIG. 2. Representative optical photomicrographs of turkestanite crystals of granites from the Papanduva Pluton: (a) turkestanite crystal (Trk) section close to (001), showing a light, clean core and dark turbid rims, between quartz (Qz) and an isotropic (Y-REE)-bearing hydrated silicate (Ysi; dark circles are EPMA spots) in a protomylonitic alkali feldspar granite. Note also narsarsukite (Nr). The crystal is mantled, along the contact with quartz, by overgrowths with a (Y-Ca)-bearing silicate, acicular aegirine (Aeg) and fluorite (Fl). Sample MR-02A. (b) Prismatic sections with basal parting among quartz (Qz), albite (Ab) and the (Y-REE)-bearing hydrated silicate. Note clean and turbid areas. Crystals occur among quartz, albite (Ab), (Y-REE)-bearing hydrated silicate. Note mantles as shown in a. Sample MR-140, plane-polarized light.

(Fig. 3b). These features are attributed mainly to metamictization phenomena and late-induced dissolution-precipitation reactions. Most turkestanite crystals are partially surrounded by a fine

mantle composed of aegirine, fluorite and an isotropic material made up of a mixture of fluorite and an (Y-HREE)-bearing hydrated silicate (Figs 2, 3).

FIG. 3. BSE images of the turkestanite crystals of the evolved peralkaline granites from the Papanduva Pluton: (a) turkestanite crystal shown in Fig. 2a with an homogeneous core and transformed and fractured rims. Note the thin irregular mantle formed by fluorite, aegirine and (Y-Ca)-bearing silicate (YCsi) along contacts with quartz, and turkestanite rims more preserved close to the contact with the (Y-REE)-bearing hydrated silicate. (b) Subhedral turkestanite crystal showing complex convolute zoning, probably due to dissolution-precipitation phenomena. Darker zones have more Th and Na, and smaller REE and Y contents than the brighter ones. Thin irregular mantles, with fluorite and aegirine also appear in contact zones with quartz. The crystal in the lower right part of the image is the (Y-REE)-bearing hydrated silicate. Sample MR-02(2). (c) Prismatic subhedral turkestanite crystals shown in Fig. 2b, associated with quartz and the (Y-REE)-bearing hydrated silicate. Mantles around the crystals are less pronounced than those found in the other samples. Sample MR-140. Mineral abbreviations as in Fig. 2.

TABLE 2. Representative WDS analyses (values expressed in oxide wt.%) and mineral formulae for turkestanite of the evolved peralkaline granites from the Papanduva Pluton.

Sample Crystal Analysis	MR 02A					MR-2(2)			MR-140				
	1					1			1	2	3		
	3, core	7, int	8, int	10, rim	11, core	1, core	2, rim	3, core	2, core	2, core	1, rim	3, rim	4, rim
SiO ₂	51.51	52.54	50.69	52.44	52.94	50.48	51.39	51.99	55.00	55.23	52.59	53.56	54.64
ThO ₂	22.00	20.27	19.26	21.49	20.30	20.77	20.96	20.91	20.94	20.60	20.91	22.38	20.95
UO ₂	0.51	0.66	0.58	1.24	0.52	0.32	0.31	0.41	0.68	0.67	1.13	0.88	0.49
Al ₂ O ₃	0.05	b.d.	0.05	0.11	0.03	0.16	0.11	0.13	0.09	0.06	0.07	0.06	0.07
La ₂ O ₃	0.90	0.87	0.91	1.03	1.11	0.89	0.85	0.51	0.71	0.70	0.86	0.71	0.76
Ce ₂ O ₃	2.50	3.06	3.43	2.41	3.74	6.80	6.01	5.80	2.66	3.17	2.50	2.98	2.80
Pr ₂ O ₃	0.47	0.24	0.08	0.44	0.38	0.37	0.52	0.65	0.34	0.58	0.40	0.16	0.79
Nd ₂ O ₃	1.37	2.00	1.71	1.23	2.01	1.67	1.28	1.13	1.82	1.60	0.96	1.74	2.14
Sm ₂ O ₃	0.13	0.21	0.26	0.25	0.24	0.19	0.34	0.36	0.58	0.51	0.36	0.27	0.41
Gd ₂ O ₃	0.18	b.d.	0.30	0.16	b.d.	0.12	0.10	0.22	0.11	0.11	b.d.	0.24	0.23
Y ₂ O ₃	0.16	0.09	0.22	0.25	0.06	0.99	0.76	0.82	0.19	0.12	0.12	0.16	0.24
Fe ₂ O ₃	0.24	0.79	1.19	0.13	1.12	0.35	0.15	b.d.	0.13	0.11	0.08	0.09	0.39
CaO	9.09	7.71	8.21	7.75	7.62	8.43	5.37	6.71	7.70	6.98	7.36	6.07	7.02
PbO	0.22	0.22	0.21	0.26	0.29	1.17	1.04	0.93	0.40	0.32	0.32	0.34	0.41
Na ₂ O	1.73	1.95	1.69	1.72	1.92	1.15	1.08	1.01	2.78	2.57	2.93	2.88	2.81
K ₂ O	2.34	2.45	2.29	2.38	2.44	0.97	1.05	1.06	3.13	3.05	2.91	2.96	3.04
Total	93.38	93.10	91.09	93.28	94.70	94.83	91.32	92.64	97.24	96.36	93.52	95.46	97.17
Structural formulae based on (Si + Al) = 8.0													
Si	7.991	8.000	7.990	7.980	7.994	7.969	7.980	7.977	7.985	7.990	7.987	7.990	7.987
Al	0.009	0.000	0.010	0.020	0.006	0.031	0.020	0.023	0.015	0.010	0.013	0.010	0.013
Sum <i>T</i>	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Th	0.776	0.702	0.691	0.744	0.697	0.746	0.741	0.730	0.692	0.678	0.723	0.760	0.697
U	0.017	0.022	0.020	0.042	0.017	0.011	0.011	0.014	0.022	0.022	0.038	0.029	0.016
Fe ³⁺	0.028	0.091	0.142	0.015	0.127	0.042	0.018	0.000	0.014	0.012	0.010	0.011	0.042
Pb	0.009	0.009	0.009	0.011	0.012	0.050	0.043	0.038	0.016	0.012	0.013	0.014	0.016
Y	0.013	0.007	0.018	0.020	0.005	0.083	0.063	0.067	0.014	0.009	0.009	0.013	0.019
<i>REE</i>	0.155	0.168	0.120	0.169	0.142	0.068	0.124	0.150	0.243	0.267	0.207	0.174	0.210
Sum <i>A</i>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
<i>REE</i>	0.156	0.184	0.261	0.136	0.268	0.509	0.389	0.333	0.083	0.082	0.072	0.154	0.166
Ca	1.511	1.258	1.387	1.264	1.233	1.426	0.894	1.103	1.198	1.082	1.198	0.969	1.099
Na	0.333	0.557	0.352	0.509	0.499	0.064	0.324	0.300	0.719	0.721	0.730	0.832	0.735
Sum <i>B</i>	2.000	2.000	2.000	1.909	2.000	2.000	1.607	1.736	2.000	1.885	2.000	1.955	2.000
Na	0.188	0.019	0.166	0.000	0.063	0.287	0.000	0.000	0.065	0.000	0.133	0.000	0.060
K	0.463	0.476	0.460	0.462	0.470	0.195	0.209	0.207	0.579	0.563	0.564	0.564	0.567
Sum <i>C</i>	0.651	0.496	0.626	0.462	0.533	0.482	0.209	0.207	0.643	0.563	0.697	0.564	0.627

b.d.: below detection limit

Mineral chemistry

Representative chemical compositions for turkestanite crystals are presented in Tables 2 (EPMA data) and 3 (LA-ICP-MS data). A full turkestanite EPMA data set (23 points) is presented in Supplementary Table 1, which has been deposited

with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Turkestanite compositions in samples MR-02A and MR-140 are relatively homogeneous (Table 2). The measured values for SiO₂, ThO₂,

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TABLE 3. Trace element composition (LA-ICP-MS) for turkestanite of the evolved peralkaline granite (Sample MR-140) from the Papanduva Pluton (concentrations and errors in ppm).

Element	Concentration	$\pm 2\sigma$ (error)	Element	Concentration	$\pm 2\sigma$ (error)
Li	3.4	0.9	La	10607	789
Be	47	27.5	Ce	26806	4536
Mg	159	14.7	Pr	3730	303
P	23	11.2	Nd	17360	1416.8
Sc	1.2	0.5	Sm	3490	247.6
Ti	96	10.9	Eu	92	7.7
Cr	3.3	2.7	Gd	2085	163.8
Mn	279	23.1	Tb	184	12.3
Cu	2.7	0.7	Dy	670	45.1
Zn	824	68.9	Ho	89	6.6
Ga	343	32.2	Er	158	12.2
Rb	107	9.8	Tm	15	1.5
Sr	256	17.6	Yb	70	7.2
Y	2419	157.1	Lu	7.0	0.8
Zr	758	60.6	Hf	22	3.2
Nb	542	43.1	Ta	18	2.0
Sn	10	1.5	Pb	5037	387.6
Cs	3.8	0.5	U	8826	705.7
Ba	1415	144.6			

V, Co, Ni, Mo and Sb gave concentrations close to the 2σ error and were omitted.

CaO, Na₂O and K₂O range between 50.5–55.3, 19.3–22.4, 6.1–10.0, 1.6–2.9 and 2.1–3.2 wt.%, respectively. The (REE+Y)₂O₃ abundances range from 5.2 to 7.5 wt.% and are relatively high for turkestanite, as discussed later. Minor oxides include Al₂O₃ (<0.1 wt. %), UO₂ (0.5–1.2%), Fe₂O₃ (0.1–1.8%) and PbO (0.2–0.4%). The greatest Al and U concentrations and the smallest Fe³⁺ concentrations are registered close to crystal rims. The total oxide contents are variable and relatively small, ranging from 91.1 to 97.2 wt.% (Table 2). As discussed by Perrault and Richard (1973) and Szymański *et al.* (1982), EPMA analyses for minerals of the ekanite–steacyite group may be problematic, as they are unstable under an electron beam (Perrault and Richard, 1973; Szymański *et al.*, 1982), and the water content is variable, giving small totals (Petersen *et al.*, 1999). Metamictization processes and related chemical transformations, expected to be extensive in ~580 Ma old crystals like those studied here, may also have allowed incorporation of additional H₂O into the turkestanite structure.

The turkestanite crystal from sample MR-02(2), with complex convolute zoning, shows larger amounts of (REE+Y)₂O₃ (9.5–11.0 wt.%) and

PbO (0.9–1.2%) and smaller amounts of UO₂ (0.3–0.4%). Ce₂O₃ contents reach values as high as 6.8 wt.%, a remarkable feature of this crystal.

The average empirical structural formulae (Table 2) shows a tetrahedral site filled mainly by Si (7.969–8.000 a.p.f.u.), with minor Al (up to 0.031). The A site is occupied by Th (0.669–0.776 a.p.f.u.), REE+Y (0.026–0.282), and minor amounts of Fe³⁺ (up to 0.212), U (0.011–0.042) and Pb (0.009–0.050). The B site contains Ca (0.894–1.695 a.p.f.u.), Na (up to 0.832) and REE (0.030–0.509). This site, as in other REE-bearing minerals of the ekanite–steacyite group (e.g. Livingstone *et al.*, 1976; Perrault and Szymański, 1982), is not always filled completely, especially in sample MR-02(2) with an occupancy as low as 1.607 a.p.f.u., where the amounts of Na are as little as 0.064 a.p.f.u. and the REE contents are as much as 0.509 a.p.f.u. The C site is partially occupied by K (0.195–0.598 a.p.f.u.) and occasionally by Na (up to 0.540 a.p.f.u.), leaving vacancies of up to 0.805, the greater values seen in the MR-02(2) sample (Table 2).

Crystals from the three samples analysed are readily distinguished by their Na and K contents

(Table 2). Sodium and K attain their largest values in sample MR-140 (0.694–0.863 a.p.f.u. Na; 0.550–0.598 a.p.f.u. K) and smallest in MR-02(2) (0.300–0.351 a.p.f.u. Na; 0.195–0.209 a.p.f.u. K), while intermediate values are found in MR-02A (0.487–0.577 a.p.f.u. Na and 0.422–0.473 a.p.f.u. K).

Substitution mechanisms

The main substitution schemes relating the end-members in the ekanite–steacyite group minerals are:

Substitution 1 correlates iraqite and theoretical *b* [$\text{Th}(\text{REE}, \text{Na})\square\text{Si}_8\text{O}_{20}$] with ekanite and the theoretical end-member *c* [$\text{REE}(\text{REE}, \text{Na})\text{KSi}_8\text{O}_{20}$], respectively, while substitutions 2 and 3 correlate steacyite with ekanite and iraqite, as well as the theoretical end-member *a* [$\text{REE}(\text{REE}, \text{Ca})\square\text{Si}_8\text{O}_{20}$] with theoretical *b* and *c*, respectively. It should be noted that substitution 3 corresponds to the combination of substitutions 1 and 2.

For turkestanite, Reguir and Chakhmouradian (1999) emphasize that some substitution of Na for Ca and REE for Th must occur, as the idealized structural formula is not charge-balanced. $\text{Th}^{4+} + \text{Na}^+ \rightleftharpoons \text{Ca}^{2+} + \text{REE}$ yields good correlation coefficients ($r^2 = 0.85$, Fig. 4) for samples

FIG. 4. Cationic REE–Ca–Na diagram for the ekanite–steacyite mineral group showing the main coupled substitution mechanisms operating in our turkestanite data set. These substitutions (substitutions 3–5) are also represented as binary cationic diagrams: $\text{Ca}^{2+} + \text{REE}^{3+}$ vs. $\text{Th}^{4+} + {}^B\text{Na}^+$ (substitution 3); ${}^B\text{Na}^+ + \text{REE}^{3+}$ vs. 2Ca^{2+} (substitution 4) and $\text{K}^+ + {}^B\text{Na}^+ + 2\text{REE}^{3+}$ vs. $2\text{Ca}^{2+} + \text{Th}^{4+} + \square$. Ekanite–steacyite group mineral data from other localities – Turkestanite data: (1) Dara-i-Pioz Complex (Pautov *et al.*, 1997); (2) Dara-i-Pioz Complex (Reguir and Chakhmouradian, 1999); (3) Jelisyiski Massif, Dzhelizu Complex (Pautov *et al.*, 1997); (4) Central Asia (Ginzburg *et al.*, 1965 as cited by Perrault and Szymański, 1982). Arapovite data: (5) Dara-i-Pioz Complex (Agakhanov *et al.*, 2004). Iraqite data: (6) Shakhi-Rash Mountain, Iraq (Livingstone *et al.*, 1976). Steacyite data: (7) Mont St. Hilaire (Richard and Perrault, 1972); (8) Central Asia (Ginzburg *et al.*, 1965 as cited by Perrault and Szymański, 1982); (9) Rouman Isle (Parodi and Della Ventura, 1987).

MR-02(A) and MR-140, demonstrating that this substitution describes the entry of the *REE* into the A site of the turkestanite structure.

The presence of *REE* at the B site is a unique feature of Papanduva turkestanite; indeed, some analyses have total ${}^B\text{REE} > {}^A\text{REE}$ (see Table 2). The entry of *REE* into the B site occurs by the substitution

which gives a good correlation with our data set ($r^2 = 0.86$) (Fig. 4). Although the dataset is limited, there is evidence for the relationship $2\text{REE}^{3+} = \text{Ca}^{2+} + \text{Th}^{4+}$ which can be used to describe *REE* entry into both A and B sites. This substitution, when combined with (3) gives substitution 4.

Figure 4 also shows a ternary diagram where the dataset for the Papanduva turkestanite are plotted together with turkestanite, arapovite, iraqite and steacyite data from other localities for comparison. When analysed as a whole, our data set plots along substitution 3, between the steacyite and iraqite end-members. Nevertheless, when the samples are considered individually, they show an alignment tendency towards ekanite that fits well with a substitution between the theoretical end-member *c* and ekanite, written as:

namely a combination of substitutions 1 and 4, with an r^2 coefficient of 0.90.

To obtain a complete description of the substitution mechanisms and end-members relevant to turkestanite crystal chemistry, we identify the dual operation of substitutions 3 and 5 which defines a final composite substitution:

This substitution mechanism was applied to a data set comprising Papanduva turkestanite analyses and compositions of turkestanite, arapovite, steacyite and iraqite from other localities worldwide (Fig. 5). All data plot inside a parallelogram formed by ekanite, theoretical end-members *b* and *c* and iraqite as its extremities, joined by straight lines representing substitutions 1 and 4. In such a parallelogram, substitution 5 corresponds to their vectorial sum. The substitution described by substitution 3 and vector $(\text{Ca}^{2+}\text{Th}^{4+}) (\text{REE}^{3+})_{-2}$ are also represented inside the parallelogram (Fig. 5a). Considering all the data, a reasonable correlation ($r^2 = 0.77$) is obtained for substitution 6. It suggests its role, as

a result of the sum of substitution mechanisms involving iraqite, steacyite, ekanite and theoretical end-member *c*, in the compositional variations observed in turkestanite (Fig. 5b).

Data for sample MR-02(2) plot away from all regression lines and were omitted, as they may represent products of late transformations (see below).

Rare earth and trace elements

Representative *REE* patterns for the Papanduva turkestanite are presented in Fig. 6. The EPMA data for samples MR-02A and MR-140 are quite coherent, though somewhat dispersed, due to low analytical precision, especially for Pr, Sm and Gd (Fig. 6a). The results for the *LREE* obtained with both EPMA and LA-ICP-MS for sample MR-140 are rather similar (Fig. 6c). The measured *REE* concentrations are 100 to 10,300 times greater

FIG. 5. Cationic $2{}^B\text{Na}^+ + \text{K}^+ + \text{REE}^{3+}$ vs. $3\text{Ca}^{2+} + \square$ diagrams for turkestanite. (a) Major coupled substitution mechanism operating in our turkestanite data set. (b) Selected analyses of turkestanite from Papanduva Pluton and turkestanite, steacyite and iraqite compositions from other localities worldwide. Symbols as in Fig. 4.

FIG. 6. Chondrite-normalized *REE* partial (EPMA data) and complete (LA-ICP-MS data) patterns for representative turkestanite of samples (a) MR-02A and MR-140, (b) MR-02(2) and (c) MR-140. Normalization factors after Boynton (1984). Y is plotted instead of Ho in a and b. Note the positive Ce anomaly in MR-02(2) (b), and the good agreement between *LMREE* measured with EPMA (grey) and LA-ICPMS (black) for sample MR-140 (c). Discussion in text.

FIG. 7. (Ce/Ce^*) vs. $\text{La}_\text{N}/\text{Sm}_\text{N}$ diagram contrasting turkestanite of sample MR-02(2) with those of MR-02A and MR-140 samples.

than the chondritic values, and the fractionation of the *LREE* over the *HREE* is strong, with $4 < \text{La}_\text{N}/\text{Y}_\text{N} < 55$, and $\text{La}_\text{N}/\text{Yb}_\text{N}$ up to 102. A negative Eu anomaly, with $\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/[(\text{Sm}_\text{N} * \text{Gd}_\text{N})^{1/2}] = 0.1$, is well developed. The fractionation pattern in the *HREE* is stronger than in the *LREE*, with $\text{Ho}_\text{N}/\text{Lu}_\text{N} = 6$ and $1 < \text{La}_\text{N}/\text{Sm}_\text{N} < 3$.

Sample MR-02(2) presents a contrasted *L-MREE* pattern, with a positive Ce anomaly, with $2.2 < \text{Ce}/\text{Ce}^* = \text{Ce}_\text{N}/[(\text{La}_\text{N} * \text{Pr}_\text{N})^{1/2}] < 2.8$, and a weaker *LREE* over *HREE* fractionation ($4 < \text{La}_\text{N}/\text{Y}_\text{N} < 7$), as well as smaller $\text{Gd}_\text{N}/\text{Y}_\text{N}$ ratios, ~ 1 –2 (Fig. 6b). Such differences are depicted on the Ce/Ce^* vs. $\text{La}_\text{N}/\text{Sm}_\text{N}$ diagram (Fig. 7). This diagram shows a well defined gap around $\text{Ce}/\text{Ce}^* = 2.1$, and a slightly negative correlation for samples MR-02A and MR-140.

The multi-element pattern obtained for a single turkestanite crystal from sample MR-140, normalized to the whole-rock composition, is shown in Fig. 8. Most of the main trace elements analysed are enriched by factors between 10 and 10^5 times (see Table 3 also). In addition Th, U and the *REE*+Y, Pb (5037 ppm), Sr (256 ppm) and Ba (1415 ppm) are the most enriched elements, while Li (3 ppm) and Rb (104), among the LILE, and Zr (758 ppm), Hf (22 ppm) and Ti (96 ppm), among the HFSE, are the most depleted. Zn (824 ppm) and Ga (343 ppm) are slightly enriched, while Mn (279 ppm) is somewhat depleted. The measured values for Be, Mg, P, Sc and Sn (not shown in Fig. 3) are 47, 159, 23, 1.2 and 10 ppm respectively; V, Co, Ni, Mo, and Sb were considered to be below detection limits.

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FIG. 8. Expanded trace-element pattern (LA-ICP-MS data) for turkestanite, normalized to the whole-rock composition. Sample MR-140.

FIG. 9. Cationic Na-Ca-K diagram for the ekanite-steacyite group. Symbols as in Fig. 4.

Discussion

The compositions for turkestanite in the granites from the Papanduva Pluton and known occurrences worldwide are compared in Table 4 and

Fig. 9. In general, our compositions are richer in Fe_2O_3 and REE_2O_3 and poorer in Al_2O_3 and ThO_2 . The K_2O , Na_2O and CaO abundances measured for samples MR-02A and MR-140

TABLE 4. Average chemical compositions (wt.% oxide) of turkestanite of peralkaline granites from the Papanduva Pluton and other localities worldwide.

Locality	Papanduva Pluton MR-02A/ MR-140 this work	Papanduva Pluton MR-02(2) this work	Dara-i-Pios Complex	Jelisyiski Massif	Central Asia (Russia)	Ilímaussaq Complex†
Reference	this work	this work	Pautov <i>et al.</i> (1997); Reguir and Chakhmouradian (1999)	Pautov <i>et al.</i> (1997)	Ginzburg <i>et al.</i> (1965)*	Petersen <i>et al.</i> (1999)
No. of analyses	22	4	5	2	2	1
SiO_2	52.79	50.93	52.68	49.64	54.55	56.67
Al_2O_3	0.07	0.16	0.32	1.03	0.74	—
ThO_2	20.68	20.60	22.14	30.97	25.11	27.70
UO_2	0.71	0.42	5.51	b.d.	1.02	—
Fe_2O_3	0.61	0.44	b.d.	0.05	0.14	—
PbO	0.30	1.03	2.23	0.20	0.23	—
REE_2O_3	6.14	9.27	2.04	b.d.	1.38	—
CaO	7.76	6.35	7.81	8.56	8.99	13.42
Na_2O	2.12	0.96	2.16	1.61	3.07	0.88
K_2O	2.60	0.92	3.48	2.43	3.69	1.33
Total	93.76	91.09	98.38	94.48	98.91	100.00

* as cited by Perrault and Szymański (1982)

† determined using a Rietveld procedure

b.d.: below detection limit

— : not analysed

overlap those observed for turkestanite from the type-locality of Dzhelelsu (Jelisyiski Massif), Kyrgystan (Pautov *et al.*, 1997), and from Central Asia (Ginzburg *et al.*, 1965) (Fig. 8). On the other hand, compositions obtained for the MR-02(2) sample reveal small K_2O , Na_2O and CaO contents (Fig. 9). The very high REE_2O_3 contents of the turkestanite from the Papanduva Pluton are noteworthy. These contents are up to three times greater than those usually found in turkestanite (Table 4, Fig. 4), and have a strong enrichment of *LREE* over *HREE*.

The Papanduva turkestanite is always associated with an unknown (*Y-REE*)-hydrated silicate. Preliminary EPMA of this unnamed silicate give up to 43 wt.% SiO_2 , 24% Y_2O_3 , 17% REE_2O_3 , 4% CaO , and 0.1% Na_2O , and a strong fractionation of the *HREE* over the *LREE* (Vilalva, 2007). This indicates the influence of crystal-chemical effects in controlling the fractionation of *REE* between the two phases during the post-magmatic crystallization stages of the Papanduva granites: the larger cations being incorporated preferentially in turkestanite and the smaller in the (*Y-REE*)-bearing hydrated silicate structural sites (e.g. Blundy and Wood, 1994).

Turkestanite sample MR-02(2) is distinct. The influence of late dissolution-reprecipitation processes is suggested by the well developed convolute zoning. Also, the REE_2O_3 concentrations are the largest (> 11 wt.%) and *REE* patterns show a strong positive Ce anomaly as well as less fractionation of *LREE* over *HREE*. Hydrothermal alteration is an important process for *REE* concentration (e.g. Mariano, 1989) and the oxidation of Ce^{3+} to Ce^{4+} should be a response to rock–fluid interaction. According to Goldberg *et al.* (1963) and German *et al.* (1995) Ce^{3+} is, unlike other trivalent *REE* ions, readily oxidized to Ce^{4+} under neutral to moderately acidic conditions and can be precipitated in the form of CeO_2 , or preferentially absorbed into mineral structures. Under oxidizing conditions the loss of trivalent *REE* from turkestanite may also lead to the observed anomaly (e.g. Zhiwei and Zhenhua, 2003). As U_3O_8 is very soluble, the smaller U content of turkestanite from sample MR-02(2) is consistent with such an interpretation.

Turkestanite crystallization conditions and controls

Textural characteristics of Papanduva turkestanite point to its post-magmatic (subsolidus) crystal-

lization in association with other Ca-bearing mineral phases such as aegirine-augite, fluorite, britholite and the undetermined (*Y-REE*)-hydrated silicate. It is believed that residual liquids of the Papanduva Pluton evolved toward progressively more peralkaline, F-rich compositions with conditions of increasing oxidation from magnetite–wüstite (MW) to hematite–magnetite (HM) buffers in the late stages. As the HFSE are more soluble in Ca-poor, F-bearing peralkaline liquids and fluids (e.g. Salvi and Williams-Jones, 1996; Salvi *et al.*, 2000), their relative concentrations increase in late- to post-magmatic stages. The post-magmatic mylonitic textures observed in the Papanduva granites containing turkestanite and HFSE-bearing minerals suggest that deformation has played an important role in the remobilization and circulation of late-stage hydrothermal fluids, in which the presence of Ca is thought to be important. Salvi and Williams-Jones (1990, 1996, 2006) and Boily and Williams-Jones (1994) studied the role of hydrothermal processes in the peralkaline rocks from the Strange Lake Complex, Labrador, Canada. They found that even minor concentrations of Ca allow fluorite crystallization, which buffers F activity to levels that prevent effective HFSE transport, leading to precipitation of HFSE-bearing minerals. Late-stage circulation of Ca-rich hydrothermal fluids, residual from magmatic crystallization and/or acquired from external sources, is well known in peralkaline rocks (e.g. Khadem Allah *et al.*, 1998; Salvi *et al.*, 2000; Schönerberger *et al.*, 2006; Vlach and Gualda, 2007; Graser and Markl, 2008). In the rocks studied here, there is no geological or petrographic evidence pointing to external fluid input, and so Ca-enrichment is attributed to the breakdown of primary Ca-bearing mineral phases, such as ferrosilite, which can be found in the less-evolved, undeformed granites. The crystallization sequence, as interpreted petrographically, indicates that Ca-rich late-stage minerals such as turkestanite and the associated (*Y-REE*)-hydrated silicate crystallized after those rich in Na and HFSE, with the f_{O_2} being buffered by the HM buffer at temperatures of ~450°C (Vilalva, 2007).

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PARTE V

ANEXOS: TABELAS DE DADOS E MAPA DE PONTOS

Tabela 1: Análises químicas em rocha-total (ICP-MS e FRX) para amostras dos Plútons Papanduva e Quiriri

Tabela 2: valores significativos de suscetibilidade magnética ($\times 10^{-3}$ SI) em amostras dos Plútons Papanduva e Quiriri

Tabela 3: Razões isotópicas Rb-Sr em amostras representativas dos Plútons Papanduva e Quiriri, Complexo Morro Redondo

Tabela 4: Razões isotópicas Sm-Nd para amostras representativas dos Plútons Papanduva e Quiriri, Complexo Morro Redondo

Tabela 5: Análises químicas WDS (% em peso de óxidos) em cristais de biotita do Plúton Quiriri

Tabela 6: Análises químicas WDS (% em peso de óxidos) para cristais de feldspato alcalino do Plúton Quiriri

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Tabela 10: Análises químicas de elementos-traços por LA-ICP-MS em cristais de britholita do Plúton Papanduva, Complexo Morro Redondo

Tabela 11: Análises químicas de elementos-traços por LA-ICP-MS de cristais de nacareniobsita do Plúton Papanduva, Complexo Morro Redondo

Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da Província Graciosa

Tabela 13: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons sieníticos e graníticos de tipo-A da associação alcalina da Província Graciosa

Tabela 14: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons graníticos de tipo-A da associação aluminosa da Província Graciosa

Tabela 15: Razões isotópicas Lu-Hf (LA-MC-ICP-MS) em cristais de zircão do Complexo Morro Redondo

Tabela 16: Valores de $^{18}\text{O}/^{16}\text{O}$ (per mil, VSMOW) em diversos minerais dos Plúton Papanduva e Quiriri, Complexo Morro Redondo

ANEXO V-17: Mapa de pontos do Complexo Morro Redondo e áreas adjacentes

Tabela 1: Análises químicas em rocha-total (ICP-MS e FRX) para amostras dos Plútons Papanduva e Quiriri

Amostra	MR 50	MR 50(A+)	MR 140	MR 02	MR 49	MR 64	MR 21	MR 01A	MR 10	MR-215	MR-62
Plúton	Papanduva										
Fácies	protomilonítica (A)							cataclástica (B)		maciça	
SiO ₂	75.70	74.55	74.84	75.38	75.16	74.79	77.78	75.98	75.52	74.53	75.40
TiO ₂	0.145	0.163	0.173	0.161	0.163	0.225	0.086	0.211	0.249	0.179	0.224
Al ₂ O ₃	10.23	9.89	10.78	10.58	10.64	10.54	11.25	10.83	10.79	11.30	11.33
Fe ₂ O ₃ ^T	4.68	5.62	3.46	3.85	3.61	3.60	1.77	2.91	3.29	3.09	2.85
MnO	0.068	0.084	0.056	0.059	0.056	0.055	0.030	0.060	0.066	0.046	0.051
MgO	0.02	0.03	0.03	0.03	0.03	0.04	0.02	0.01	0.01	0.05	0.10
CaO	0.12	0.15	0.22	0.23	0.24	0.21	0.13	0.26	0.27	0.28	0.35
Na ₂ O	4.98	5.24	4.77	4.68	4.57	4.47	4.22	4.34	4.07	4.58	4.21
K ₂ O	4.03	3.77	4.52	4.33	4.45	4.44	4.75	4.66	4.62	4.69	4.71
P ₂ O ₅	0.007	0.007	0.007	0.008	0.008	0.006	0.008	0.009	0.011	0.012	0.015
LOI	0.28	0.34	0.28	0.32	0.30	0.42	0.22	0.44	0.28	0.20	0.20
Total	100.26	99.84	99.14	99.63	99.23	98.80	100.26	99.71	99.18	98.96	99.44
Fe#	0.995	0.994	0.990	0.991	0.991	0.988	0.988	0.996	0.997	0.982	0.962
ASI	0.801	0.762	0.820	0.826	0.833	0.840	0.913	0.856	0.885	0.861	0.895
Al	1.23	1.28	1.18	1.17	1.16	1.15	1.07	1.12	1.08	1.12	1.06
Li		178.6		73.2			24.7	29.7		38.6	31.8
Be		9.40		11.0			6.41	7.90		7.93	6.57
Ga*	38	36	31	33	30	31	32	30	30	32	29
Zn*	303	347	200	199	156	180	89	147	169	135	114
Rb		302		195			147	136		130	123
Sr		4.77		4.92			1.66	5.22		11.0	16.0
Y		323		165			145	168		170	112
Zr*	2030	2428	1482	1798	689	1054	748	1217	1376	776	781
Zr		2697		2168			882	1569		763	741
Nb		88.1		52.4			21.3	65.5		48.0	45.6
Cs		1.25		1.34			0.51	1.61		9.39	0.76
Ba		16.2		28.5			4.22	40.0		83.7	144
La		119		94.1			200	164		104	188
Ce		233		177			268	274		231	297
Pr		30.1		21.8			32.4	32.5		24.4	34.6
Nd		119		82.8			113	120		91.1	120
Sm		31.8		20.1			21.7	26.1		21.1	23.6
Eu		1.34		0.80			0.76	1.01		0.92	1.07
Gd		39.1		21.7			20.5	26.2		21.4	20.6
Tb		6.78		3.78			3.05	4.46		3.63	3.23
Dy		43.0		24.3			17.5	28.2		21.8	18.7
Ho		9.19		5.27			3.44	5.93		4.54	3.78
Er		26.1		15.7			9.49	17.1		12.5	10.6
Tm		3.73		2.31			1.31	2.48		1.81	1.53
Yb		24.1		15.4			8.40	15.9		11.6	10.1
Lu		3.46		2.29			1.22	2.21		1.57	1.41
Hf		61.2		46.4			19.4	33.7		22.1	19.6
Pb		88.3		39.5			21.2	50.1		42.7	24.1
Th		47.9		32.4			22.2	42.1		32.4	26.9
U		7.81		6.20			2.01	4.43		3.70	3.28
Tsat(zr)	1029	1041	993	1020	908	957	933	978	999	924	932
Tsat(ap)	740	730	732	746	744	721	768	760	770	767	792
A		5.7		4.2			2.5	4.5		3.6	3.1

Tabela 1: Análises químicas em rocha-total (ICP-MS e FRX) para amostras dos Plútons Papanduva e Quiriri

Amostra	MR 32	MR 39	MR 01D	MR-161	MR-164	MR-202	MR-178	MR-174	MR-17	MR-201A	MR-245B
Plúton	Papanduva			Quiriri							
Fácies	maciça		microgr. (D)	Q1							
SiO ₂	76.04	75.91	73.99	75.74	75.06	75.37	75.37	74.90	74.40	75.06	75.24
TiO ₂	0.137	0.219	0.109	0.178	0.196	0.183	0.178	0.191	0.184	0.201	0.205
Al ₂ O ₃	10.79	11.52	11.34	12.59	12.67	12.54	12.53	12.91	12.63	12.66	12.89
Fe ₂ O ₃ ^T	3.65	2.91	3.75	1.47	1.47	1.37	1.37	1.40	1.39	1.50	1.46
MnO	0.045	0.042	0.054	0.027	0.026	0.021	0.023	0.025	0.025	0.023	0.026
MgO	0.03	0.07	0.03	0.14	0.16	0.15	0.14	0.16	0.16	0.20	0.15
CaO	0.21	0.20	0.26	0.53	0.69	0.66	0.64	0.68	0.62	0.70	0.75
Na ₂ O	4.97	4.14	4.65	3.52	3.43	3.46	3.42	3.44	3.54	3.53	3.51
K ₂ O	4.08	4.74	4.69	5.10	5.13	5.15	5.15	5.27	5.20	5.16	5.16
P ₂ O ₅	0.007	0.016	0.004	0.021	0.026	0.021	0.022	0.024	0.019	0.027	0.029
LOI	0.48	0.50	0.30	0.44	0.46	0.42	0.46	0.52	0.52	0.46	0.64
Total	100.44	100.27	99.18	99.76	99.32	99.35	99.30	99.52	98.69	99.52	100.06
fe#	0.991	0.974	0.991	0.904	0.892	0.891	0.898	0.887	0.886	0.871	0.897
ASI	0.832	0.936	0.859	1.026	1.018	1.006	1.013	1.025	1.004	1.000	1.013
Al	1.17	1.04	1.12	0.90	0.88	0.90	0.89	0.88	0.91	0.90	0.88
Li	65.1	30.0	84.4	11.5	17.7	7.98	10.1	13.6	4.22	22.4	
Be	8.34	5.87	5.72	3.04	3.35	3.36	5.57	3.53	2.79	4.28	
Ga*	32	28	38	18	19	19	19	20	19	20	18
Zn*	200	114	158	29	25	24	22	26	35	24	34
Rb	151	104	132	138	132	134	137	155	138	136	
Sr	5.68	5.46	2.32	57.7	61.3	56.6	54.9	60.1	53.1	56.4	
Y	303	71.4	59.8	45.6	45.5	48.3	42.8	125	61.7	43.8	
Zr*	1174	708	523	170	183	176	167	176	179	178	188
Zr	1419	883	618	167	169	163	194	173	165	196	
Nb	55.8	44.3	21.5	20.8	22.0	20.5	18.3	19.3	19.0	23.2	
Cs	0.64	0.40	0.59	1.13	1.38	1.02	1.26	1.46	1.44	1.51	
Ba	20.9	81.0	4.57	647	712	648	640	710	693	700	
La	168	90.3	31.3	73.9	74.2	70.4	66.7	285	87.7	71.7	
Ce	237	123	63	148	150	144	112	423	172	117	
Pr	41.9	18.1	8.79	13.3	13.5	13.0	12.4	45.5	16.3	13.2	
Nd	180	63.9	35.3	43.1	44.6	42.1	40.3	146	54.2	43.6	
Sm	51.2	11.9	8.96	7.68	8.18	7.55	7.37	25.8	10.2	8.04	
Eu	2.14	0.55	0.32	0.62	0.71	0.62	0.66	1.61	0.81	0.72	
Gd	56.3	10.6	9.35	7.01	7.47	6.97	6.78	21.9	9.58	7.42	
Tb	8.77	1.76	1.50	1.16	1.21	1.17	1.11	3.26	1.59	1.18	
Dy	50.0	11.3	9.27	7.00	7.07	7.13	6.66	18.4	9.57	6.94	
Ho	9.48	2.46	1.95	1.49	1.48	1.56	1.43	3.65	2.05	1.45	
Er	23.5	7.68	5.92	4.44	4.22	4.60	4.09	9.92	5.83	4.21	
Tm	2.91	1.20	0.95	0.66	0.61	0.67	0.61	1.38	0.86	0.63	
Yb	17.9	8.55	7.37	4.48	4.13	4.52	4.07	8.88	5.55	4.25	
Lu	2.58	1.30	1.27	0.65	0.59	0.66	0.59	1.21	0.78	0.62	
Hf	31.2	19.8	13.1	5.72	5.84	5.47	6.53	6.39	5.85	7.42	
Pb	61.5	18.3	12.6	30.8	24.1	27.2	23.5	25.9	36.4	23.5	
Th	37.9	26.1	11.4	24.5	24.4	23.5	23.0	30.5	25.1	28.0	
U	4.85	2.89	1.27	3.94	2.73	2.94	2.56	3.34	2.25	2.78	
Tsat(zr)	968	928	880	797	802	798	794	799	799	798	804
Tsat(ap)	743	801	688	821	832	817	821	824	800	835	842
A	4.3	3.0	1.6	3.2	2.9	2.9	2.7	3.5	2.8	3.1	

Tabela 1: Análises químicas em rocha-total (ICP-MS e FRX) para amostras dos Plútons Papanduva e Quiriri

Amostra	MR-193	MR-185	MR-186A	MR-15	MR-247D	MR-247C	MR-180B	MR-250	MR-201B
Plúton	Quiriri								
Fácies	Q2						Q4		enclave
SiO ₂	75.21	75.38	75.41	73.35	75.50	74.82	70.47	77.00	72.12
TiO ₂	0.189	0.202	0.193	0.233	0.145	0.203	0.267	0.076	0.353
Al ₂ O ₃	12.60	12.44	12.92	13.34	12.62	12.91	12.87	11.26	13.77
Fe ₂ O ₃ ^T	1.43	1.51	1.03	1.64	1.89	1.54	1.97	1.56	2.59
MnO	0.028	0.033	0.016	0.020	0.062	0.024	0.055	0.024	0.061
MgO	0.19	0.16	0.12	0.32	0.01	0.19	0.21	0.01	0.49
CaO	0.69	0.63	0.59	0.97	0.45	0.77	0.77	0.35	1.08
Na ₂ O	3.46	3.46	3.47	3.94	3.91	3.47	3.55	1.56	3.85
K ₂ O	5.15	5.11	5.27	4.73	4.96	5.17	4.99	7.20	4.91
P ₂ O ₅	0.023	0.024	0.024	0.054	0.019	0.032	0.049	0.006	0.075
LOI	0.34	0.46	0.58	0.87	0.72	0.62	4.67	0.70	0.30
Total	99.31	99.41	99.62	99.47	100.29	99.75	99.87	99.74	99.60
fe#	0.871	0.894	0.885	0.822	0.994	0.879	0.894	0.996	0.826
ASI	1.006	1.006	1.035	0.998	1.000	1.016	1.018	1.024	1.012
Al	0.89	0.90	0.88	0.87	0.94	0.88	0.87	0.92	0.85
Li	22.1	8.02	26.0						36.4
Be	3.24	3.78	3.35						7.98
Ga*	19	19	18	17	23	17	17	21	19
Zn*	25	46	31	23	38	27	64	35	61
Rb	130	135	143						164
Sr	54.9	55.3	52.0						71.8
Y	48.9	40.7	88.9						53.4
Zr*	183	174	182	186	343	171	237	210	300
Zr	198	176	190						327
Nb	21.3	17.3	21.5						25.6
Cs	1.54	1.27	1.46						2.26
Ba	624	651	694						902
La	71.8	73.9	215						74.5
Ce	148	145	251						154
Pr	13.4	13.5	34.0						14.4
Nd	43.8	44.1	109						49.2
Sm	7.97	7.83	19.1						9.32
Eu	0.64	0.67	1.58						0.95
Gd	7.23	6.75	15.3						8.26
Tb	1.21	1.07	2.25						1.34
Dy	7.29	6.24	12.5						7.93
Ho	1.55	1.32	2.46						1.68
Er	4.51	3.77	6.86						4.91
Tm	0.68	0.55	0.98						0.75
Yb	4.57	3.66	6.49						5.20
Lu	0.67	0.53	0.91						0.74
Hf	6.87	5.80	6.67						8.25
Pb	26.0	40.8	27.6						37.6
Th	24.1	22.5	25.9						26.6
U	2.54	3.15	3.91						4.90
Tsat(zr)	801	797	804	799	860	796	823	820	843
Tsat(ap)	823	828	828	878	811	846	841	742	897
A	2.8	2.8	3.3						3.6

Tabela 2: valores significativos de suscetibilidade magnética ($\times 10^{-3}$ SI) em amostras dos Plútons Papanduva e Quiriri

Plúton		Papanduva			Quiriri			
Fácies	protomilonítica (n = 302)	cataclástica (n = 207)	microgranítica (n = 162)	Q1 (n = 280)	Q2 (n = 67)	Q3 (n = 30)	Q4 (n = 11)	
valor máximo	0.870	12.800	2.490	6.910	6.750	2.190	4.700	
valor mínimo	0.032	0.066	0.019	0.173	0.041	0.525	1.060	
valor médio	0.148	2.068	0.269	2.633	2.831	1.171	3.066	
desvio padrão	0.120	3.194	0.574	1.441	1.939	0.499	1.274	
mediana	0.120	0.238	0.088	2.565	2.920	1.100	2.570	
moda	0.104	-	0.035	3.380	2.830	1.440	-	

Tabela 3: Razões isotópicas Rb-Sr em amostras representativas dos Plútons Papanduva e Quiriri, Complexo Morro Redondo

Pluton	Fácies	Amostra	Rb (ppm)	Sr (ppm)	1/Sr	$\text{Sr}^{87}/\text{Sr}^{86}$ (Y)	$\text{Rb}^{87}/\text{Sr}^{86}$ (X)	T(Ma) $\lambda = 1.42$	$(\text{Sr}^{87}/\text{Sr}^{86})_i$ p/T(Ma)	$\epsilon_{(0)}$	T_{DM} (Ma)	$\epsilon_{(TDM)}$	T_1 (Ma)	$\epsilon_{(T1)}$
Papanduva	cataclástica	MR-01A	159.4	5.2	0.191	1.4	93.8	580	1.4	9173.0	485.4	-28.1	580	-1830.6
	protomilonítica	MR-50(A+)	292.4	5.5	0.183	2.3	179.2	580	0.8	22676.8	626.0	-27.2	580	1650.7
	microgranítica	MR-01D	149.0	2.8	0.361	2.2	178.7	580	0.7	21588.2	597.9	-27.4	580	624.1
Quiriri	Q1	MR-174	175.0	63.4	0.016	0.8	8.0	580	0.7	919.0	587.9	-27.4	580	-14.6
	Q1	MR-17	138.0	53.1	0.019	0.8	7.6	580	0.7	930.4	631.7	-27.1	580	51.7
	Q2	MR-193	135.8	57.9	0.017	0.8	6.8	580	0.7	915.2	689.2	-26.8	580	123.3

Tabela 4: Razões isotópicas Sm-Nd para amostras representativas dos Plútons Papanduva e Quiriri, Complexo Morro Redondo

Pluton	Fácies	Amostra	Sm (ppm)	Nd (ppm)	Sm/Nd	1/Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	$\epsilon_{(0)}$	$f_{\text{Sm/Nd}}$	T_{DM} (Ma)	$\epsilon_{(\text{TDM})}$	T_1 (Ma)	$\epsilon_{(T1)}$
Papanduva	cataclástica	MR-01A	26.1	120.0	0.218	0.008	0.1315	0.511562	-21.0	-0.33	2776	2.09	580.0	-16.2
	microgranítica	MR-01D	9.0	35.3	0.254	0.028	0.1535	0.511673	-18.8	-0.22	3587	0.95	580.0	-15.6
	maciça	MR-39	11.9	63.9	0.186	0.016	0.1126	0.511482	-22.5	-0.43	2362	2.80	580.0	-16.3
	protomilonítica	MR-50(A+)	31.8	119.0	0.267	0.008	0.1616	0.511704	-18.2	-0.18	4145	0.35	580.0	-15.6
Quiriri	Q1	MR-17	10.2	54.2	0.188	0.018	0.1138	0.511279	-26.5	-0.42	2714	2.19	580.0	-20.4
	Q1	MR-174	25.8	146.0	0.177	0.007	0.1069	0.511265	-26.8	-0.46	2551	2.46	580.0	-20.1
	Q2	MR-186A	19.1	109.0	0.175	0.009	0.1060	0.511325	-25.6	-0.46	2442	2.65	580.0	-18.9
	Q2	MR-193	8.0	43.8	0.182	0.023	0.1100	0.511260	-26.9	-0.44	2640	2.31	580.0	-20.5

Tabela 5: Análises químicas WDS (% em peso de óxidos) em cristais de biotita do Plúton Quiriri

[illegible]

Tabela 5: Análises químicas WDS (% em peso de óxidos) em cristais de biotita do Plúton Quiriri

Amostra	MR-193	MR-193	MR-193	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-19A	MR-19A	MR-19A	MR-19A	MR-19A	MR-19A
Cristal	6			1	2 (enclave)	3 (enclave)	4 (enclave)		5 (enclave)		6 (enclave)			c.1-1	c.3-1	c.1-2	c.2-1	c.2-4	c.2-4
Ponto	2-n	1-b	2-n	1-b	2-n	1-n	1-n	1-b	2-n	1-b	2-n	1-b	2-n	pto 1 -n	pto 2 -b	pto 1 -n	pto 1 -b	pto 1 -i	pto 2 -b
SiO ₂	36.032	36.768	36.308	37.049	36.138	37.474	35.106	34.498	35.637	35.738	35.738	35.131	35.980	37.155	36.881	36.855	36.932	36.188	35.922
TiO ₂	3.721	3.166	3.653	3.073	3.740	2.641	3.471	3.966	3.254	2.950	3.321	4.169	4.373	3.003	2.826	2.926	2.990	4.091	3.164
Al ₂ O ₃	12.725	13.091	12.778	12.586	12.694	12.771	13.484	13.207	12.778	13.286	13.100	13.698	13.196	11.653	12.620	11.527	11.693	12.524	12.349
V ₂ O ₅	0.000	0.000	0.000	0.000	0.101	0.000	0.054	0.000	0.188	0.098	0.000	0.000	0.048						
FeO	26.149	25.860	25.959	26.110	26.699	25.025	25.575	26.023	25.979	26.441	26.109	25.408	24.889	24.517	21.268	24.351	24.330	25.524	25.102
MnO	0.312	0.398	0.371	0.290	0.238	0.336	0.281	0.470	0.404	0.316	0.380	0.525	0.488	0.361	0.204	0.257	0.265	0.259	0.263
MgO	7.100	7.303	7.262	7.935	7.023	8.414	7.266	7.091	7.857	7.368	7.272	6.959	7.622	8.291	10.412	8.243	9.013	7.481	7.183
CaO	0.052	0.000	0.000	0.000	0.000	0.000	0.063	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ZnO	0.074	0.082	0.107	0.042	0.090	0.000	0.092	0.106	0.071	0.097	0.056	0.000	0.000	0.000	0.000	0.000	0.000	0.048	0.063
BaO	0.336	0.122	0.075	0.087	0.260	0.070	1.222	1.536	0.188	0.211	0.142	1.453	0.816	0.000	0.195	0.146	0.000	0.264	0.160
Na ₂ O	0.067	0.065	0.068	0.051	0.039	0.048	0.059	0.075	0.080	0.000	0.060	0.049	0.053	0.075	0.079	0.082	0.057	0.069	0.082
K ₂ O	9.292	9.714	9.443	9.982	9.441	9.225	9.163	8.966	9.384	9.301	9.366	9.072	9.059	8.930	9.174	8.844	8.155	8.891	9.019
Cl	0.301	0.323	0.425	0.370	0.329	0.288	0.382	0.372	0.340	0.344	0.367	0.343	0.312	0.832	0.950	1.211	0.693	0.377	0.829
F	0.958	1.020	0.981	0.547	0.418	0.437	0.359	0.424	0.421	0.591	0.382	0.427	0.721	0.449	0.245	0.264	0.290	0.250	0.331
Total	97.119	97.912	97.430	98.122	97.210	96.729	96.577	96.734	96.581	96.741	96.293	97.234	97.557	95.266	94.854	94.706	94.418	95.966	94.467
Si	5.699	5.750	5.716	5.766	5.689	5.837	5.583	5.518	5.639	5.654	5.666	5.552	5.625	5.907	5.804	5.912	5.875	5.716	5.798
AlIV	2.301	2.250	2.284	2.234	2.311	2.163	2.417	2.482	2.361	2.346	2.334	2.448	2.375	2.093	2.196	2.088	2.125	2.284	2.202
Fe	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
sum T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
AlVI	0.070	0.162	0.087	0.075	0.044	0.182	0.111	0.007	0.021	0.132	0.114	0.103	0.057	0.091	0.144	0.092	0.067	0.047	0.147
Ti	0.443	0.372	0.432	0.360	0.443	0.309	0.415	0.477	0.387	0.351	0.396	0.495	0.514	0.359	0.334	0.353	0.358	0.486	0.384
V	0.000	0.000	0.000	0.000	0.011	0.000	0.006	0.000	0.020	0.010	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000
Fe	3.459	3.382	3.418	3.398	3.515	3.260	3.402	3.481	3.438	3.499	3.462	3.358	3.254	3.260	2.799	3.267	3.237	3.372	3.388
Mn	0.042	0.053	0.049	0.038	0.032	0.044	0.038	0.064	0.054	0.042	0.051	0.070	0.065	0.049	0.027	0.035	0.036	0.035	0.036
Mg	1.674	1.702	1.704	1.841	1.648	1.953	1.722	1.690	1.853	1.738	1.718	1.639	1.776	1.965	2.442	1.971	2.137	1.761	1.728
Zn	0.009	0.009	0.012	0.005	0.010	0.000	0.011	0.013	0.008	0.011	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.008
Sum Y	5.696	5.681	5.703	5.716	5.702	5.749	5.704	5.731	5.781	5.783	5.748	5.665	5.671	5.723	5.747	5.718	5.835	5.706	5.691
Ba	0.021	0.007	0.005	0.005	0.016	0.004	0.076	0.096	0.012	0.013	0.009	0.090	0.050	0.000	0.012	0.009	0.000	0.016	0.010
Ca	0.009	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.021	0.020	0.021	0.015	0.012	0.014	0.018	0.023	0.025	0.000	0.018	0.015	0.016	0.023	0.024	0.026	0.018	0.021	0.026
K	1.875	1.938	1.896	1.982	1.896	1.833	1.859	1.829	1.894	1.877	1.894	1.829	1.807	1.811	1.842	1.810	1.655	1.791	1.857
Sum X	1.925	1.965	1.922	2.002	1.924	1.852	1.964	1.949	1.930	1.890	1.921	1.934	1.873	1.834	1.878	1.845	1.672	1.829	1.893
Cl	0.081	0.086	0.113	0.098	0.088	0.076	0.103	0.101	0.091	0.092	0.099	0.092	0.083	0.224	0.253	0.329	0.187	0.101	0.227
F	0.479	0.504	0.488	0.269	0.208	0.215	0.181	0.214	0.211	0.296	0.192	0.213	0.357	0.226	0.122	0.134	0.146	0.125	0.169
Soma-Cát.	15.621	15.646	15.624	15.719	15.626	15.600	15.668	15.680	15.712	15.673	15.669	15.599	15.544	15.557	15.624	15.562	15.507	15.535	15.583
Soma-O	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000

Tabela 5: Análises químicas WDS (% em peso de óxidos) em cristais de biotita do Plúton Quiriri

[illegible]

Tabela 5: Análises químicas WDS (% em peso de óxidos) em cristais de biotita do Plúton Quiriri

Amostra	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-218B	MR-180B	MR-180B	MR-15A	MR-15A	MR-15A
Cristal	c5-1 encl maf		c6-1 gr hosp		c7-1 encl maf		c8-1 gr, interst		c7-2 encl maf		c2-1		c6-1		c6-2	
Ponto	3-i	1-b	2-n	1-b	2-n	1-b	2-n	1-b	2-n	1-b	2-n	1-b	2-n	1-b	2-n	1-n
SiO ₂	36.76	37.76	37.95	36.42	35.58	36.93	36.43	36.95	36.90	35.08	36.03	36.16	36.23	35.31	34.06	34.90
TiO ₂	2.50	2.30	2.74	3.27	4.41	2.83	2.81	2.47	3.02	2.48	2.40	3.85	3.80	4.26	3.96	4.01
Al ₂ O ₃	12.79	13.40	13.02	13.00	13.24	12.76	12.77	12.68	12.29	14.04	13.08	13.04	12.78	13.50	12.63	12.69
V ₂ O ₅																
FeO	23.50	20.36	20.54	25.34	26.76	24.73	25.39	25.54	26.14	25.64	25.14	26.05	25.37	26.11	26.92	25.92
MnO	0.44	0.38	0.37	0.24	0.23	0.44	0.41	0.33	0.30	0.44	0.41	0.33	0.37	0.17	0.13	0.18
MgO	10.45	13.00	13.00	8.55	8.15	9.33	8.98	9.21	9.05	9.15	9.25	8.70	8.59	8.52	8.38	7.95
CaO	0.01	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.06	0.08	0.02	0.03	0.06	0.05	0.01
ZnO	0.06	0.08	0.14	0.05	0.11	0.00	0.04	0.04	0.05	0.01	0.01	0.03	0.07	0.01	0.00	0.01
BaO	0.14	0.12	0.24	0.09	0.95	0.04	0.14	0.04	0.05	0.05	0.04	0.04	0.07	0.99	1.01	0.89
Na ₂ O	0.00	0.01	0.08	0.22	0.21	0.03	0.04	0.05	0.04	0.04	0.03	0.05	0.06	0.08	0.05	0.12
K ₂ O	9.34	9.87	9.87	9.73	9.34	9.62	9.41	9.49	9.58	8.92	9.27	9.44	9.22	8.85	8.87	9.04
Cl	0.30	0.15	0.10	0.34	0.31	0.20	0.34	0.32	0.31	0.29	0.34	0.28	0.30	0.18	0.11	0.13
F	1.04	1.41	1.07	1.58	1.47	0.56	0.41	1.23	0.36	0.92	0.99	0.99	0.45	0.34	0.12	0.00
Total	97.33	98.83	99.12	98.85	100.77	97.47	97.17	98.35	98.09	97.12	97.06	98.97	97.32	98.37	96.28	95.84
Si	5.713	5.697	5.699	5.667	5.492	5.728	5.694	5.743	5.721	5.514	5.662	5.591	5.647	5.480	5.443	5.556
AlIV	2.287	2.303	2.301	2.333	2.409	2.272	2.306	2.257	2.247	2.486	2.338	2.376	2.348	2.470	2.379	2.381
Fe	0.000	0.000	0.000	0.000	0.100	0.000	0.000	0.000	0.032	0.000	0.000	0.034	0.005	0.050	0.178	0.062
sum T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
AlVI	0.056	0.080	0.004	0.052	0.000	0.061	0.046	0.066	0.000	0.114	0.084	0.000	0.000	0.000	0.000	0.000
Ti	0.292	0.261	0.310	0.383	0.512	0.330	0.331	0.288	0.352	0.293	0.284	0.447	0.445	0.497	0.476	0.480

Tabela 6: Análises químicas WDS (% em peso de óxidos) para cristais de feldspato alcalino do Plúton Quiriri

Amostra	MR-180B	MR-180B	MR-180B	MR-250	MR-250	MR-250	MR-180B	MR-180B	MR-180B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B
Cristal	c4-1			c2-1			c1-1 mtz	c1-2 mtz	c1-3 mtz	c4-1 20um						
Ponto	p1-n	p2-i	p3-b	p1-b	p2-i	p3-n	p1-b	p1-n	p1-n	p1-b	p2-i	p4-i	p5-n	p1-b	p2-i	p3-n
SiO ₂	63.97	64.17	63.97	75.70	63.54	64.09	62.36	62.17	62.83	64.51	65.10	64.57	64.55	64.00	64.43	65.17
TiO ₂	0.04	0.03	0.00	0.00	0.07	0.00	0.00	0.05	0.00	0.07	0.00	0.00	0.00	0.01	0.00	0.01
Al ₂ O ₃	18.78	18.90	18.81	13.26	18.57	18.74	18.32	18.26	18.34	19.03	18.90	19.00	18.85	18.53	18.90	19.08
Fe ₂ O ₃	0.06	0.17	0.02	0.00	0.00	0.00	0.08	0.10	0.14	0.07	0.08	0.11	0.13	0.10	0.05	0.14
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.03	0.06	0.00	0.00	0.03
MgO	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00
CaO	0.17	0.14	0.16	0.03	0.00	0.03	0.06	0.07	0.10	0.11	0.20	0.16	0.18	0.10	0.09	0.06
Na ₂ O	4.58	2.99	2.06	2.03	0.39	1.49	1.49	0.67	1.35	4.08	5.35	3.96	4.25	1.35	2.39	5.15
K ₂ O	11.03	12.60	14.01	9.12	16.69	15.68	14.74	15.75	14.51	11.01	9.09	11.07	10.57	15.06	13.50	9.22
BaO	0.40	0.53	0.84	0.06	0.00	0.09	0.19	0.23	0.26	0.21	0.20	0.25	0.18	0.10	0.21	0.14
SrO																
Total	99.05	99.52	99.86	100.21	99.26	100.10	97.25	97.32	97.53	99.12	98.93	99.15	98.75	99.26	99.59	98.99
Fórmula estrutural com base em 32 O																
Si	11.825	11.851	11.857	13.260	11.888	11.868	11.865	11.863	11.896	11.860	11.904	11.871	11.890	11.910	11.887	11.899
Al	4.092	4.114	4.109	2.738	4.094	4.089	4.108	4.106	4.091	4.124	4.074	4.117	4.092	4.063	4.108	4.105
Felll	0.008	0.024	0.003	0.000	0.001	0.000	0.011	0.014	0.019	0.010	0.011	0.015	0.018	0.014	0.007	0.019
Sum T	15.925	15.989	15.969	15.998	15.983	15.957	15.984	15.984	16.007	15.994	15.989	16.004	15.999	15.988	16.002	16.023
Ti	0.006	0.004	0.000	0.000	0.009	0.000	0.000	0.008	0.000	0.009	0.000	0.000	0.000	0.002	0.000	0.002
Mn	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.002	0.002	0.004	0.009	0.000	0.000	0.004
Mg	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.002	0.001	0.001	0.000	0.000	0.000	0.003	0.000
Ca	0.033	0.027	0.032	0.005	0.000	0.005	0.012	0.015	0.020	0.022	0.039	0.032	0.036	0.021	0.018	0.011
Na	1.643	1.070	0.739	0.689	0.143	0.533	0.551	0.248	0.496	1.456	1.897	1.413	1.516	0.489	0.856	1.823
K	2.601	2.967	3.313	2.038	3.983	3.704	3.578	3.835	3.504	2.583	2.120	2.596	2.483	3.576	3.178	2.149
Ba	0.029	0.038	0.061	0.004	0.000	0.006	0.014	0.017	0.019	0.015	0.014	0.018	0.013	0.007	0.015	0.010
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.317	4.106	4.144	2.737	4.135	4.248	4.157	4.127	4.042	4.089	4.073	4.063	4.056	4.094	4.070	3.999
Soma-Cát.	20.242	20.095	20.113	18.735	20.118	20.206	20.141	20.111	20.049	20.083	20.062	20.067	20.055	20.081	20.072	20.023
Soma-O	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000

Tabela 6: Análises químicas WDS (% em peso de óxidos) para cristais de feldspato alcalino do Plúton Quiriri

Amostra	MR-201B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B
Cristal	c1-1 20um							c7-1 20 um					
Ponto	p4-n	p1-b	p2-b	p3-i	p4-i	p5-n	p6-n	p1-b	p2-b	p3-i	p4-i	p5-n	p6-n
SiO ₂	64.54	65.01	66.06	65.07	65.71	63.99	65.31	64.08	65.11	65.16	64.48	65.09	64.73
TiO ₂	0.00	0.00	0.05	0.01	0.00	0.00	0.00	0.05	0.00	0.00	0.04	0.00	0.00
Al ₂ O ₃	18.80	19.08	19.04	19.07	19.19	19.21	19.58	18.73	18.73	18.84	18.98	19.00	18.91
Fe ₂ O ₃	0.02	0.14	0.12	0.16	0.17	0.07	0.13	0.06	0.12	0.11	0.12	0.10	0.15
MnO	0.00	0.02	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.04
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.01	0.00	0.00	0.01
CaO	0.12	0.13	0.13	0.06	0.12	0.09	0.14	0.07	1.25	0.11	0.16	0.12	0.00
Na ₂ O	4.90	3.64	5.92	2.70	4.08	2.75	5.94	2.07	6.25	3.05	2.81	4.01	3.86
K ₂ O	10.42	11.75	8.71	13.49	11.33	13.09	9.11	14.07	7.72	12.83	13.21	11.49	11.80
BaO	0.14	0.00	0.09	0.11	0.20	0.16	0.08	0.11	0.02	0.07	0.12	0.15	0.21
SrO													
Total	98.94	99.76	100.13	100.68	100.81	99.37	100.31	99.23	99.22	100.17	99.92	99.96	99.70
Si	11.876	11.883	11.912	11.872	11.884	11.822	11.797	11.887	11.850	11.913	11.853	11.882	11.874
Al	4.076	4.110	4.046	4.101	4.090	4.182	4.169	4.095	4.018	4.058	4.113	4.089	4.088
Felll	0.002	0.019	0.016	0.022	0.023	0.010	0.017	0.008	0.017	0.014	0.016	0.014	0.020
Sum T	15.954	16.011	15.974	15.995	15.997	16.015	15.983	15.989	15.885	15.986	15.981	15.985	15.982
Ti	0.000	0.000	0.007	0.002	0.000	0.000	0.000	0.007	0.000	0.000	0.006	0.000	0.000
Mn	0.000	0.003	0.001	0.000	0.003	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.007
Mg	0.001	0.000	0.000	0.000	0.000	0.001	0.005	0.000	0.002	0.001	0.001	0.000	0.002
Ca	0.023	0.025	0.024	0.012	0.024	0.018	0.027	0.013	0.244	0.021	0.032	0.023	0.000
Na	1.748	1.289	2.070	0.955	1.430	0.986	2.082	0.745	2.207	1.081	1.000	1.420	1.371
K	2.446	2.738	2.004	3.141	2.613	3.085	2.098	3.330	1.791	2.992	3.099	2.676	2.762
Ba	0.010	0.000	0.007	0.008	0.014	0.012	0.006	0.008	0.002	0.005	0.008	0.011	0.015
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.228	4.056	4.114	4.117	4.084	4.102	4.218	4.103	4.246	4.101	4.146	4.130	4.157
Soma-Cát.	20.182	20.067	20.087	20.112	20.081	20.117	20.200	20.092	20.132	20.087	20.127	20.115	20.139
Soma-O	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000	32.000

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C
Cristal	c4-1 mtz	c4-1 mtz	c8-1 gd zon	c8-1 gd zon	c8-1 gd zon	c8-1 gd zon	c8-1 gd zon	c8-1 gd zon	c8-1 gd zon	c10-1 pq zon	c10-1 pq zon	c10-1 pq zon	c12-1 zon
Ponto	p1-b	p2-n	p1-b	p2-i/b	p3-i/n	p4-n	p5-i/n	p6-i/b	p7-b	p1-b	p2-i	p3-n	p1-b
SiO ₂	64.11	63.09	62.69	62.91	62.14	60.93	61.55	61.70	60.86	60.72	62.07	62.03	63.94
TiO ₂	0.00	0.04	0.00	0.00	0.08	0.03	0.00	0.05	0.00	0.00	0.00	0.00	0.01
Al ₂ O ₃	22.40	23.09	22.97	23.00	23.62	24.23	24.09	23.98	24.46	25.78	24.04	23.96	22.57
Fe ₂ O ₃	0.13	0.09	0.07	0.16	0.25	0.17	0.31	0.22	0.18	0.13	0.22	0.16	0.21
MnO	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01
CaO	2.74	3.59	3.56	3.60	4.46	5.20	4.98	4.44	5.26	4.14	4.60	4.77	2.52
Na ₂ O	10.15	9.57	9.47	9.27	8.67	8.29	8.36	8.59	8.28	8.32	8.94	8.83	9.63
K ₂ O	0.33	0.40	0.51	1.02	1.02	0.91	0.96	1.05	0.84	0.52	0.68	0.70	0.55
BaO	0.00	0.00	0.00	0.07	0.00	0.12	0.03	0.16	0.22	0.02	0.00	0.02	0.00
SrO													
Total	99.89	99.89	99.27	100.05	100.22	99.87	100.28	100.20	100.12	99.63	100.56	100.49	99.44
fórmula estrutural com base em 32 O													
Si	11.336	11.182	11.182	11.172	11.031	10.883	10.935	10.973	10.852	10.794	10.978	10.982	11.340
Al	4.669	4.823	4.830	4.814	4.941	5.101	5.045	5.026	5.140	5.401	5.011	5.000	4.718
FeIII	0.018	0.011	0.010	0.021	0.033	0.023	0.042	0.029	0.024	0.017	0.030	0.021	0.028
Sum T	16.022	16.016	16.022	16.007	16.005	16.007	16.022	16.027	16.016	16.212	16.018	16.004	16.086
Ti	0.000	0.005	0.000	0.000	0.011	0.004	0.000	0.007	0.000	0.000	0.000	0.000	0.002
Mn	0.002	0.003	0.000	0.001	0.000	0.000	0.000	0.001	0.003	0.000	0.000	0.002	0.000
Mg	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.002	0.000	0.002
Ca	0.519	0.682	0.680	0.685	0.848	0.995	0.948	0.845	1.005	0.789	0.871	0.905	0.478
Na	3.481	3.289	3.274	3.192	2.985	2.869	2.878	2.963	2.863	2.869	3.067	3.032	3.310
K	0.075	0.091	0.117	0.232	0.231	0.207	0.218	0.238	0.191	0.119	0.153	0.159	0.124
Ba	0.000	0.000	0.000	0.005	0.000	0.008	0.002	0.011	0.015	0.002	0.000	0.001	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.076	4.070	4.072	4.115	4.074	4.083	4.047	4.067	4.077	3.779	4.094	4.099	3.917
Soma-Cát.	20.099	20.086	20.094	20.122	20.079	20.090	20.069	20.094	20.093	19.991	20.112	20.103	20.003

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-247C	MR-245B	MR-245B	MR-245B	MR-245B	MR-218B	MR-218B	MR-218B
Cristal	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c12-1 zon	c4-1 encl maf	c4-1 encl maf	c4-2 encl maf
Ponto	p2-i/b	p3-i/n	p4-n	p5-i/n	p6-i/b	p7-b	p1-b	p2-i/b	p3-i/n	p4-n	p1-b	p2-i	p1-i
SiO ₂	61.24	62.88	63.08	62.93	61.50	64.00	64.03	63.01	61.59	62.02	64.47	65.11	60.29
TiO ₂	0.00	0.00	0.00	0.00	0.04	0.00	0.05	0.00	0.04	0.04	0.00	0.05	0.00
Al ₂ O ₃	24.31	23.42	23.33	23.10	24.38	22.55	22.86	23.44	23.16	23.52	21.89	21.99	24.72
Fe ₂ O ₃	0.27	0.07	0.13	0.22	0.34	0.11	0.15	0.16	0.23	0.13	0.15	0.23	0.32
MnO	0.00	0.02	0.01	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.03	0.00	0.01
MgO	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.01
CaO	5.54	4.44	4.36	4.32	5.43	3.30	3.62	4.32	4.35	4.28	2.50	2.43	5.55
Na ₂ O	8.15	8.57	8.78	8.78	8.34	9.54	9.33	8.79	8.27	8.50	9.95	10.10	8.31
K ₂ O	0.64	1.02	1.05	0.95	0.55	0.69	0.73	1.07	1.46	0.94	0.43	0.38	0.16
BaO	0.00	0.00	0.03	0.01	0.08	0.06	0.00	0.09	0.11	0.12	0.00	0.00	0.07
SrO													
Total	100.14	100.42	100.77	100.32	100.66	100.25	100.79	100.89	99.20	99.56	99.41	100.30	99.45
Si	10.887	11.118	11.127	11.144	10.883	11.300	11.250	11.107	11.067	11.067	11.434	11.443	10.790
Al	5.093	4.881	4.849	4.822	5.085	4.692	4.734	4.870	4.904	4.947	4.576	4.555	5.214
FeIII	0.035	0.009	0.018	0.029	0.045	0.015	0.020	0.021	0.031	0.018	0.020	0.030	0.043
Sum T	16.015	16.008	15.994	15.995	16.014	16.006	16.004	15.999	16.002	16.033	16.030	16.027	16.047
Ti	0.000	0.000	0.000	0.000	0.005	0.000	0.007	0.000	0.005	0.005	0.000	0.007	0.000
Mn	0.000	0.002	0.002	0.000	0.000	0.000	0.003	0.001	0.000	0.000	0.005	0.000	0.002
Mg	0.002	0.002	0.000	0.000	0.000	0.001	0.000	0.002	0.000	0.002	0.000	0.002	0.004
Ca	1.056	0.841	0.824	0.820	1.029	0.624	0.681	0.816	0.838	0.818	0.474	0.458	1.064
Na	2.809	2.939	3.002	3.015	2.861	3.267	3.180	3.006	2.880	2.941	3.421	3.442	2.884
K	0.144	0.230	0.236	0.216	0.124	0.156	0.163	0.240	0.335	0.214	0.097	0.084	0.037
Ba	0.000	0.000	0.002	0.001	0.006	0.004	0.000	0.006	0.008	0.009	0.000	0.000	0.005
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.011	4.014	4.065	4.051	4.025	4.052	4.033	4.071	4.066	3.989	3.997	3.994	3.996
Soma-Cát.	20.026	20.021	20.059	20.046	20.039	20.058	20.037	20.070	20.068	20.022	20.027	20.021	20.042

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-218B	MR-218B	MR-218B	MR-156B	MR-156B	MR-156B	MR-156B	MR-156B	MR-156B	MR-156B	MR-186A	MR-186A	MR-186A
Cristal	c4-2 encl maf	c4-3 encl maf	c4-3 encl maf	c4-1	c4-1	c4-1	c6-1	c6-1	c1-1 tx graf	c1-1 tx graf	c1-1 zon	c1-1 zon	c1-1 zon
Ponto	p2-n	p1-i	p2-n	p1-b	p2-i	p3-n	p1-b	p2-n	p1-b	p2-n	p1-b	p2-i/b	p3-i
SiO ₂	61.10	61.40	62.41	67.71	68.24	68.00	67.60	68.59	67.43	67.63	63.46	64.38	63.75
TiO ₂	0.00	0.03	0.00	0.05	0.11	0.00	0.01	0.05	0.00	0.03	0.03	0.00	0.03
Al ₂ O ₃	23.97	23.77	23.04	19.97	20.10	20.37	20.25	20.03	19.88	20.33	23.40	22.90	23.40
Fe ₂ O ₃	0.38	0.30	0.42	0.18	0.01	0.15	0.13	0.03	0.00	0.04	0.24	0.13	0.18
MnO	0.03	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00
MgO	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
CaO	4.78	4.20	3.87	0.01	0.12	0.11	0.10	0.03	0.19	0.13	3.83	3.45	4.19
Na ₂ O	8.72	9.24	9.12	11.39	11.79	11.81	11.78	12.03	11.48	11.59	9.38	9.42	8.98
K ₂ O	0.19	0.17	0.21	0.10	0.07	0.18	0.04	0.04	0.07	0.05	0.31	0.61	0.57
BaO	0.00	0.07	0.00	0.00	0.05	0.10	0.00	0.00	0.00	0.03	0.10	0.00	0.00
SrO													
Total	99.15	99.19	99.07	99.41	100.49	100.72	99.92	100.80	99.05	99.85	100.74	100.91	101.08
Si	10.940	10.988	11.149	11.898	11.879	11.832	11.839	11.902	11.896	11.844	11.156	11.281	11.168
Al	5.058	5.013	4.850	4.135	4.125	4.178	4.180	4.095	4.134	4.196	4.848	4.729	4.832
FeIII	0.051	0.041	0.056	0.023	0.002	0.020	0.018	0.004	0.000	0.005	0.032	0.017	0.023
Sum T	16.049	16.042	16.055	16.056	16.006	16.030	16.037	16.001	16.029	16.045	16.036	16.027	16.023
Ti	0.000	0.003	0.000	0.007	0.014	0.000	0.002	0.007	0.000	0.003	0.003	0.000	0.003
Mn	0.004	0.002	0.000	0.002	0.002	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000
Mg	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000
Ca	0.916	0.806	0.741	0.001	0.022	0.020	0.018	0.006	0.036	0.025	0.721	0.648	0.786
Na	3.027	3.206	3.157	3.879	3.979	3.986	3.998	4.046	3.928	3.934	3.197	3.198	3.049
K	0.043	0.038	0.048	0.023	0.015	0.040	0.008	0.008	0.016	0.012	0.069	0.137	0.127
Ba	0.000	0.005	0.000	0.000	0.003	0.007	0.000	0.000	0.000	0.002	0.007	0.000	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	3.991	4.062	3.946	3.912	4.035	4.052	4.027	4.067	3.980	3.981	3.996	3.987	3.965
Soma-Cát.	20.040	20.104	20.001	19.967	20.041	20.082	20.064	20.069	20.009	20.025	20.033	20.014	19.988

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-186A	MR-186A	MR-186A	MR-186A	MR-186A	MR-186A	MR-180B	MR-180B	MR-201B	MR-201B	MR-201B	MR-201B	MR-201B
Cristal	c1-1 zon	c1-1 zon	c1-1 zon	c1-1 zon	c1-1 zon	c1-1 zon	c7-1 mtz	c7-1 mtz	c2-1	c2-1	c2-1	c2-1	c2-1
Ponto	p4-i/n	p5-n	p6-i/n	p7-i	p8-i/b	p9-b	p1-b	p2-n	p1-b	p2-i	p3-n	p4-i	p5-b
SiO ₂	63.23	63.02	63.42	63.29	63.67	64.84	67.45	67.83	65.23	64.41	62.88	63.44	63.65
TiO ₂	0.03	0.04	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.07	0.00	0.00	0.00
Al ₂ O ₃	23.16	23.71	23.05	23.46	23.40	22.77	20.82	20.31	21.70	22.50	23.02	22.38	22.16
Fe ₂ O ₃	0.20	0.12	0.35	0.23	0.25	0.16	0.31	0.15	0.15	0.21	0.17	0.22	0.16
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.01	0.01	0.00	0.00
CaO	3.92	4.26	3.76	4.31	3.98	3.26	0.34	0.45	2.49	3.48	4.10	4.04	3.11
Na ₂ O	9.18	9.43	9.30	8.92	9.34	10.01	11.16	11.14	9.95	9.31	8.87	9.09	9.67
K ₂ O	0.70	0.33	0.70	0.68	0.48	0.31	0.46	0.13	0.59	0.72	0.54	0.66	0.39
BaO	0.00	0.03	0.06	0.04	0.00	0.00	0.00	0.03	0.08	0.00	0.00	0.00	0.00
SrO													
Total	100.42	100.95	100.63	100.94	101.11	101.36	100.58	100.05	100.19	100.71	99.58	99.83	99.15
Si	11.165	11.074	11.182	11.127	11.157	11.306	11.757	11.853	11.487	11.315	11.180	11.261	11.340
Al	4.820	4.912	4.789	4.860	4.833	4.679	4.277	4.184	4.504	4.659	4.823	4.683	4.652
FelII	0.027	0.016	0.047	0.030	0.033	0.021	0.040	0.020	0.019	0.027	0.022	0.030	0.021
Sum T	16.012	16.002	16.018	16.017	16.022	16.006	16.075	16.057	16.010	16.001	16.025	15.974	16.013
Ti	0.003	0.005	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.009	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.001	0.000	0.001	0.003
Mg	0.001	0.001	0.000	0.000	0.000	0.001	0.006	0.000	0.002	0.002	0.002	0.000	0.001
Ca	0.742	0.802	0.710	0.811	0.747	0.610	0.063	0.084	0.469	0.655	0.781	0.768	0.593
Na	3.143	3.214	3.180	3.041	3.175	3.385	3.770	3.776	3.397	3.170	3.056	3.130	3.341
K	0.158	0.074	0.157	0.153	0.107	0.069	0.101	0.029	0.133	0.162	0.123	0.148	0.087
Ba	0.000	0.002	0.004	0.003	0.000	0.000	0.000	0.002	0.006	0.000	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.047	4.099	4.051	4.008	4.029	4.065	3.944	3.891	4.006	3.998	3.962	4.048	4.025
Soma-Cát.	20.059	20.101	20.069	20.025	20.051	20.071	20.019	19.947	20.016	19.999	19.987	20.022	20.038

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-168A	MR-168A	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B	MR-245B
Cristal	c1-1	c3-1	c7-1	c7-1	c7-1	c7-1	c7-1	c7-1	c7-1	c10-1	c10-1	c10-1	c11-1
Ponto	p1-n	p1-b	p1-b	p2-i	p3-n	p4-n/i	p5-i	p6-b	p1-b	p2-i	p3-n	p1-b	p2-i
SiO ₂	66.83	67.81	66.15	64.90	64.48	66.32	66.21	65.83	66.85	65.43	64.68	65.44	64.58
TiO ₂	0.00	0.00	0.01	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.01
Al ₂ O ₃	19.66	19.73	20.97	22.42	22.09	21.23	22.02	21.74	20.86	21.53	21.67	21.16	21.99
Fe ₂ O ₃	0.03	0.06	0.27	0.17	0.21	0.24	0.16	0.15	0.19	0.21	0.08	0.09	0.21
MnO	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.01	0.00	0.01	0.00
MgO	0.00	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.15	0.17	1.64	3.13	2.90	2.09	2.65	2.20	1.64	2.66	2.56	1.69	2.86
Na ₂ O	11.76	11.77	10.73	9.55	9.45	10.41	10.28	10.43	10.26	9.53	9.94	10.46	9.31
K ₂ O	0.04	0.02	0.56	0.75	0.70	0.52	0.64	0.67	0.95	1.14	1.13	0.70	0.99
BaO	0.01	0.05	0.03	0.03	0.05	0.03	0.04	0.08	0.00	0.00	0.00	0.00	0.00
SrO													
Total	98.47	99.61	100.39	100.95	99.93	100.87	101.99	101.12	100.75	100.50	100.05	99.59	99.95
Si	11.878	11.910	11.614	11.365	11.396	11.587	11.468	11.499	11.683	11.506	11.444	11.579	11.416
Al	4.119	4.084	4.339	4.628	4.601	4.372	4.495	4.475	4.297	4.462	4.518	4.413	4.582
FeIII	0.004	0.008	0.036	0.022	0.028	0.032	0.020	0.019	0.024	0.027	0.010	0.012	0.028
Sum T	16.001	16.002	15.989	16.015	16.025	15.991	15.983	15.992	16.004	15.995	15.973	16.003	16.026
Ti	0.000	0.000	0.002	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.002
Mn	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.003	0.000	0.001	0.000	0.002	0.000
Mg	0.001	0.001	0.005	0.001	0.002	0.002	0.001	0.001	0.000	0.000	0.000	0.000	0.001
Ca	0.028	0.033	0.309	0.588	0.550	0.392	0.491	0.412	0.307	0.502	0.486	0.321	0.542
Na	4.052	4.006	3.654	3.241	3.239	3.528	3.453	3.531	3.476	3.248	3.410	3.587	3.190
K	0.009	0.004	0.126	0.168	0.158	0.115	0.141	0.150	0.212	0.256	0.255	0.158	0.222
Ba	0.000	0.003	0.002	0.002	0.003	0.002	0.003	0.005	0.000	0.000	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.090	4.047	4.098	4.000	3.957	4.042	4.088	4.102	3.996	4.007	4.151	4.074	3.957
Soma-Cát.	20.091	20.049	20.087	20.014	19.982	20.033	20.071	20.095	20.001	20.002	20.124	20.077	19.983

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-245B	MR-201B	MR-201B	MR-201B	MR-201B	MR-19B	MR-19B	MR-19B	MR-19B	MR-19B	MR-19B	MR-19B	MR-19B
Cristal	c11-1	c7-1 fenocr	c7-1 fenocr	c7-1 fenocr	c7-1 fenocr	c.3-1	c.3-1	c.3-1	c.3-1	c.3-2	c.3-2	c.3-2	c.3-3
Ponto	p3-n	p1-b	p2-i	p3-i/n	p4-n	pto 1 -b	pto 2 -i	pto 3 -n	pto 4 -n	pto 1 -b	pto 2 -i	pto 3 -n	pto 1 -b
SiO ₂	62.74	63.33	61.95	63.50	63.44	66.15	63.56	63.71	63.22	65.46	64.21	65.20	66.47
TiO ₂	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.02	0.02	0.00	0.04	0.01	0.00
Al ₂ O ₃	22.97	23.14	23.37	22.65	23.04	20.77	22.77	22.55	22.52	21.56	22.20	21.82	20.78
Fe ₂ O ₃	0.19	0.22	0.29	0.27	0.36	0.12	0.18	0.13	0.19	0.08	0.18	0.21	0.10
MnO	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.06	0.00	0.00	0.02	0.03	0.00
MgO	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.01
CaO	4.00	4.12	4.79	3.41	4.01	2.43	4.11	4.16	4.15	2.86	3.60	3.37	2.04
Na ₂ O	8.99	8.90	8.59	9.35	9.18	8.67	8.07	8.04	7.79	8.77	8.54	8.30	8.96
K ₂ O	0.68	0.66	0.91	0.60	0.75	1.40	0.57	0.60	0.87	0.40	0.44	0.44	0.39
BaO	0.00	0.00	0.00	0.00	0.10								
SrO													
Total	99.60	100.36	99.91	99.78	100.88	99.53	99.30	99.26	98.78	99.13	99.22	99.38	98.74
Si	11.167	11.179	11.038	11.261	11.170	11.693	11.286	11.318	11.297	11.577	11.393	11.514	11.757
Al	4.819	4.815	4.908	4.733	4.780	4.326	4.765	4.720	4.743	4.494	4.642	4.543	4.331
FelII	0.026	0.029	0.039	0.035	0.048	0.016	0.024	0.017	0.026	0.010	0.024	0.028	0.014
Sum T	16.013	16.024	15.985	16.029	15.999	16.034	16.075	16.055	16.066	16.081	16.059	16.085	16.102
Ti	0.000	0.000	0.002	0.000	0.000	0.000	0.004	0.003	0.003	0.000	0.005	0.001	0.000
Mn	0.002	0.000	0.000	0.002	0.000	0.000	0.000	0.009	0.000	0.000	0.002	0.004	0.000
Mg	0.005	0.000	0.000	0.000	0.002	0.000	0.000	0.002	0.005	0.001	0.000	0.001	0.002
Ca	0.763	0.778	0.914	0.648	0.757	0.459	0.782	0.791	0.794	0.541	0.683	0.638	0.386
Na	3.102	3.044	2.966	3.216	3.134	2.971	2.778	2.768	2.700	3.005	2.938	2.843	3.073
K	0.155	0.149	0.207	0.136	0.168	0.316	0.130	0.136	0.198	0.091	0.100	0.099	0.087
Ba	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	4.026	3.972	4.089	4.001	4.068	3.746	3.694	3.707	3.699	3.638	3.730	3.585	3.548
Soma-Cát.	20.038	19.995	20.073	20.031	20.067	19.780	19.769	19.762	19.765	19.719	19.789	19.670	19.650

Tabela 7: Análises químicas WDS (% em peso de óxidos) para cristais de plagioclásio do Plúton Quiriri

Amostra	MR-19B	MR-19B	MR-19B	MR-18	MR-18	MR-18	MR-18	MR-18	MR-18	MR-18
Cristal	c.3-3	c.3-3	c.3-3	c.4-1	c.4-1	c.4-1	c.3-1	c.3-1	c.3-1	c.3-1
Ponto	pto 2 -i	pto 3 -i	pto 4 -n	pto 1 -b	pto 2 -n	pto 3 -i	pto 1 -b	pto 2 -i	pto 3 -n	pto 4 -i
SiO ₂	65.52	64.71	63.82	68.31	68.23	67.85	69.04	68.88	68.96	68.75
TiO ₂	0.00	0.01	0.04	0.00	0.00	0.00	0.05	0.00	0.00	0.00
Al ₂ O ₃	21.78	22.36	23.04	19.69	19.65	19.77	19.63	19.45	19.66	19.58
Fe ₂ O ₃	0.16	0.17	0.18	0.10	0.00	0.02	0.07	0.07	0.02	0.07
MnO	0.01	0.00	0.00	0.00	0.05	0.03	0.01	0.05	0.00	0.01
MgO	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00
CaO	3.18	3.91	4.64	0.55	0.39	0.16	0.18	0.27	0.46	0.29
Na ₂ O	8.69	8.28	7.72	9.74	9.36	9.80	10.10	10.08	9.96	10.22
K ₂ O	0.34	0.33	0.40	0.17	0.54	0.50	0.05	0.09	0.06	0.13
BaO										
SrO										
Total	99.67	99.76	99.83	98.56	98.23	98.14	99.12	98.89	99.12	99.04
Si	11.535	11.404	11.262	12.031	12.057	12.016	12.076	12.085	12.066	12.056
Al	4.518	4.644	4.791	4.087	4.092	4.126	4.047	4.022	4.055	4.046
FeIII	0.021	0.022	0.024	0.013	0.000	0.003	0.009	0.009	0.003	0.009
Sum T	16.074	16.071	16.077	16.131	16.149	16.144	16.131	16.116	16.123	16.110
Ti	0.000	0.001	0.005	0.000	0.000	0.000	0.006	0.000	0.000	0.000
Mn	0.001	0.000	0.000	0.000	0.007	0.005	0.001	0.007	0.000	0.001
Mg	0.000	0.000	0.000	0.001	0.004	0.001	0.000	0.000	0.000	0.000
Ca	0.599	0.738	0.877	0.104	0.073	0.030	0.034	0.052	0.087	0.054
Na	2.966	2.830	2.643	3.327	3.207	3.365	3.425	3.428	3.379	3.475
K	0.077	0.074	0.090	0.038	0.123	0.113	0.010	0.021	0.013	0.030
Ba	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum M	3.643	3.642	3.614	3.471	3.413	3.515	3.477	3.508	3.479	3.559
Soma-Cát.	19.717	19.713	19.692	19.602	19.562	19.659	19.608	19.624	19.602	19.669

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR39	MR39	MR39	MR39	MR039-1-1	MR039-1-2	MR039-2-1	MR039-2-2	MR039-4-1	MR039-5-2	MR039-6-1	MR039-6-2	MR-39-3-1	MR-39-2-2	MR-39-4-3	MR-39c5-1
local_spot	AnC1P1- b	AnC2P1 b	AnC2P2 n	AnC6P1 b	n	b	n	b	n	b	n	b	interm-b	inter	inter	inter
Facies	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça
Li	408.32	405.6	435.63	1120.22	271.41	248.48	330.79	256.33	482.89	1209.64	720.47	980.81	345.02	1052.69	726.56	662.16
Be	32.99	28.38	14.16	85.43												
P	33.61	37.86	93.71	29.69												
Ca	3.33	3.33	3.59	3.33	25014.54	25014.54	25014.54	25014.54	25014.54	25014.54	25014.54	25014.54	25014.53	25014.53	25014.53	25014.53
Sc	4.73	15.35	15.36	16.16	9.73	11.7	17.11	13.21	6.73	5.95	13.51	10.55	13.57	18.68	11.75	33.52
Ti	13707.48	12052.75	14026.6	22009.48	10902.86	11171.5	13842.99	9513.82	14689.76	16882.24	15672.27	21827.15	12887.17	14119.1	15611.81	7543.01
V	11.17	28.88	33.15	23.84	16.66	19.93	30.87	23.62	8.65	4.77	19.81	8.53	19.22	26.13	13.73	46.45
Cr	7.52	9.6	10.64	11.31	4.27	6.15	8.19	8.1	3.28	<2.04	4.67	4.76	11.08	8.21	8.38	13.73
Mn	5011.89	5718.29	5459.62	9489.7									264.5	<0.41	1123.53	468.16
Co	4.23	5.56	5.41	8.14	5.56	5.68	7.61	5.34	4.7	4.85	5.24	8.2	2.97	2.58	4.04	2.84
Ni	1.82	3.03	4.73	4.72	<1.66	<1.77	<2.02	<1.55	<1.57	<1.62	<1.66	<2.34	<2.80	<2.77	<3.80	<2.61
Cu	15.87	1.51	2.1	2.54	0.54	0.46	1.1	0.75	0.41	0.54	0.56	0.96	0.51	0.322	2.85	0.8
Zn	2204.13	2037.25	2034.85	3791.65									1220.16	1486.8	1816.82	895.39
Ga	12.21	14.12	17.11	11.75	13.16	12.44	20.87	13.08	12.36	11.51	11.47	14.18	13.07	10.23	12.78	8.66
Rb	29.81	18.04	24.46	36.74	12.09	15.67	16.56	10.72	19.08	24.64	29.09	39.4	18.1	24.95	57.62	27.4
Sr	25.87	22.1	18.56	64.64	21.63	17.55	14.21	13.86	25.03	24.01	29.66	78.36	32.62	37.75	74.46	18.32
Y	112.02	78.87	335.78	265.34	87.46	92.59	126.11	65.69	173.7	212.52	202.33	435.86	124.7	218.35	262.85	78.4
Zr	419.3	296.75	295.78	475.95	261.13	317.04	377.55	198.26	461.46	708.48	512.55	1573.51	264.06	579.3	1218.67	288.17
Nb	100.24	79.47	97.98	334.88	55.72	65.41	76.34	53.59	86.94	135.97	170.52	498.27	72.51	222.66	314.72	45.64
Mo	0.6	0.5	0.58	0.65												
Sn	32.41	17.38	14.43	19.81	10.82	11.61	8.57	7.71	22.43	20.86	29.78	73.73	17.89	32.88	30.63	10.2
Sb	0.116	<0.044	<0.032	0.203												
Cs	3.1	0.184	0.836	0.129	0.0166	<0.0068	0.022	0.0651	0.735	0.0114	<0.0074	0.0425	0.471	<0.0189	12.49	8.11
Ba	7.23	8.25	18.31	16.78	2.365	1.174	12	3.92	1.773	1.15	2.1	10.6	6.19	2.57	42.49	20.44
La	21.05	30.9	73.11	25.14	18.65	14.08	66.44	20.49	13.83	14.04	15.56	28.86	15.49	18.43	19.71	16.6
Ce	47.24	71.02	109.47	46.76	57.18	52.93	92.2	70.27	43.06	50.9	48.9	60.03	52.45	48	37.7	41.69
Pr	8.47	12.05	26.06	7.23	10.41	9.64	25.47	12.22	7.78	9.53	7.89	8.9	10.17	7.16	5.88	7.05
Nd	37.17	52.76	106.67	29.58	50.99	48.07	94.51	55.34	37.87	48.76	36.19	36.61	50.36	30.55	23.77	30.91
Sm	9.82	15.12	30.76	5.92	15.53	15.58	23.25	17.12	10.97	18.41	12.04	10.38	16.3	8.3	6.59	7.56
Eu	0.494	0.622	1.36	0.294	0.638	0.646	1.13	0.68	0.392	0.77	0.545	0.452	0.595	0.417	0.404	0.337
Gd	7.9	12.58	31.75	6.16	14.56	14.52	24.91	14.76	10.66	18.1	12.52	13.23	14.21	11.27	7.95	6.21
Tb	1.434	1.87	5.45	1.35	2.14	2.19	4.35	2.19	1.73	3.01	2.26	2.67	2.41	2.03	1.52	0.94
Dy	13.23	14.12	46.04	18.97	15.2	15.7	25.49	16.4	16.92	26.08	20.75	30.3	18.56	21.8	18.04	8.88
Ho	4.26	3.47	9.72	7.82	3.86	4.2	5.45	3.55	6.17	8.36	7.07	12.92	4.94	7.11	7.24	2.95
Er	22.52	16.32	32.79	50.57	18.19	19.82	20.47	12.31	34.16	43.9	39.5	84.68	24.65	41.04	50.65	17.61
Tm	6.45	4.13	5.8	14.75	4.52	4.94	4.43	3.04	9.02	11.67	10.78	27.26	5.88	10.55	13.69	4.36
Yb	70.63	44.65	48.46	135.74	46.5	51.81	42.29	35.04	92.52	121.03	112.9	308.68	60.4	102.75	126.43	47.53
Lu	13.82	9.4	8.74	24.5	9.64	10.6	8.53	7.75	17.95	24.65	21.07	57.3	11.76	19.1	22.08	10.43
Hf	16.11	9.8	9.32	18.84	10.3	13.33	11.85	7.51	17.47	27.87	18	74.74	9.12	21.79	30.41	9.15
Ta	1.572	1.127	1.449	4.52	0.98	1.26	1.34	0.95	1.52	2.2	2.4	8.05	1.01	3.15	5.44	1.05
Pb	35.81	37.3	55.23	79.06	14.31	13.72	19.42	52.78	26.3	24.42	31.67	63.44	35.48	26.18	53.6	15.79
Th	3.24	1.463	8.1	6.38	0.74	0.259	6.38	3.3	0.87	0.0314	0.059	1.22	1.54	0.049	3.29	0.213
U	1.883	0.048	2.38	0.201	0.0114	0.0183	0.21	0.0663	0.0594	0.00435	0.0052	0.0573	0.163	0.0036	0.253	0.188

protomil = protomilonítica; catac= cataclástica; microgran = microgranítica. b = borda; n = núcleo; inter = zona intermediária

Erro 2 sigma (2σ)

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR39	MR39	MR39	MR39	MR039-1-1	MR039-1-2	MR039-2-1	MR039-2-2	MR039-4-1	MR039-5-2	MR039-6-1	MR039-6-2	MR-39-3-1	MR-39-2-2	MR-39-4-3	MR-39c5-1
local_spot	AnC1P1- b	AnC2P1 b	AnC2P2 n	AnC6P1 b	n	b	n	b	n	b	n	b	interm-b	inter	inter	inter
Facies	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça
Li	59.42	60.44	66.64	175.6	47.64	44.52	60.96	48.64	102.82	294.42	183.66	261.94	132.76	423.56	335.06	319.28
Be	19.5	16.98	8.84	51.48	0	0	0	0	0	0	0	0	0	0	0	0
P	7.34	8.22	19.44	7.8	0	0	0	0	0	0	0	0	0	0	0	0
Ca	0.22	0.22	0.24	0.22	1600.22	1599.56	1639.54	1599.38	1600.54	1602.6	1603.3	1613.1	1657.26	1661.84	1686.9	1650.76
Sc	0.52	1.42	1.46	1.6	1.14	1.38	2.1	1.64	0.92	0.92	2.16	1.78	3.7	5.32	3.86	11.5
Ti	1782.36	1623.78	1960.4	3194.28	2881.32	2992.32	3783.38	2662.98	4524.98	5820.96	5616.92	8131.52	3596	4117.24	5209.62	2630.76
V	0.9	2.2	2.56	1.92	4.16	5.06	8	6.3	2.56	1.6	6.88	3.1	2.82	3.96	2.36	8.2
Cr	1.62	1.8	1.94	2.36	2.82	3.7	5.14	4.68	2.52	1.8	3.56	4.12	4.68	4.74	6.16	4.72
Mn	419.3	488.12	476.68	849.6	0	0	0	0	0	0	0	0	32.58	1.04	163	70.74
Co	0.54	0.7	0.7	1.06	1.46	1.52	2.08	1.5	1.46	1.7	1.9	3.1	0.44	0.4	0.66	0.48
Ni	0.42	0.56	0.8	0.82	3.82	2.9	2.36	3.26	4.86	5.28	5.98	7.82	2.32	2.36	3.18	2.26
Cu	1.9	0.34	0.44	0.54	0.28	0.26	0.6	0.42	0.26	0.38	0.4	0.72	0.22	0.184	0.94	0.3
Zn	230.02	218.66	225.1	432.72	0	0	0	0	0	0	0	0	243.66	308.92	426.7	218.84
Ga	1.3	1.5	1.86	1.36	7	6.64	11.24	7.16	7.3	7.44	7.66	9.76	3	2.46	3.48	2.46
Rb	2.96	1.84	2.56	3.96	4.54	5.92	6.36	4.2	8.18	11.72	14.32	20.1	2.78	3.96	10.14	5
Sr	2.46	2.14	1.86	6.54	10.6	8.76	7.64	7.24	14.06	15.04	19.22	52.42	15.6	18.16	37.68	11.32
Y	10.98	7.94	34.66	28.24	12.34	13.34	18.7	10.02	29.8	41.8	41.7	94.22	17.02	30.94	42.06	13.06
Zr	42.3	30.76	31.56	52.28	56.7	70.58	86.82	47.24	125.58	224.18	170.74	551.88	60.74	139.58	339.74	84.36
Nb	12.94	10.6	13.52	47.76	4.62	5.46	6.54	4.62	8	13.58	17.58	53.04	13.52	43.32	69.96	10.6
Mo	0.22	0.194	0.22	0.24	0	0	0	0	0	0	0	0	0	0	0	0
Sn	4.22	2.38	2.06	2.9	3.02	3.28	2.5	2.28	7.28	7.58	11.24	28.92	1.88	3.32	3.44	1.3
Sb	0.07	0.05	0.04	0.094	0	0	0	0	0	0	0	0	0	0	0	0
Cs	0.3	0.036	0.102	0.032	0.0064	0.006	0.0116	0.0154	0.168	0.007	0.0064	0.0162	0.186	0.017	5.86	4
Ba	1.1	1.24	2.64	2.54	0.2	0.102	1.04	0.34	0.168	0.12	0.22	1.14	1.36	0.6	11.06	5.54
La	2.22	3.32	8.04	2.88	4.58	3.56	17.32	5.54	4.28	5.08	5.92	11.58	3.76	4.7	5.82	5.14
Ce	4.38	6.72	10.6	4.68	11.52	10.92	19.64	15.48	10.78	14.76	14.9	19.24	17.26	16.56	15.02	17.42
Pr	0.68	0.96	2.08	0.62	2.2	2.1	5.72	2.84	2.06	2.96	2.58	3.06	1.78	1.3	1.22	1.52
Nd	4.44	6.32	12.94	3.92	12.36	11.98	24.36	14.8	11.66	17.56	13.74	14.68	5.68	3.6	3.16	4.18
Sm	1.38	2.04	4.12	0.98	3.9	4.02	6.22	4.76	3.52	6.94	4.8	4.38	5.18	2.8	2.58	3.08
Eu	0.1	0.114	0.2	0.082	0.138	0.142	0.26	0.16	0.108	0.24	0.182	0.16	0.18	0.136	0.154	0.13
Gd	1.04	1.48	3.4	0.94	2.36	2.4	4.28	2.6	2.14	4.2	3.06	3.4	6.3	5.24	4.28	3.5
Tb	0.196	0.24	0.7	0.2	0.44	0.46	0.94	0.48	0.44	0.9	0.72	0.88	0.6	0.54	0.46	0.3
Dy	1.74	1.88	6.04	2.68	1.78	1.88	3.16	2.06	2.38	4.16	3.46	5.3	4.5	5.52	5.26	2.72
Ho	0.4	0.32	0.86	0.72	0.3	0.34	0.46	0.3	0.54	0.78	0.68	1.3	1	1.5	1.74	0.74
Er	2.42	1.82	3.66	5.76	1.58	1.72	1.86	1.12	3.3	4.62	4.3	9.52	9.6	16.76	23.98	8.76
Tm	0.62	0.42	0.6	1.48	0.64	0.7	0.66	0.46	1.5	2.18	2.1	5.54	2.22	4.16	6.18	2.06
Yb	7.8	5.14	5.76	16.22	5.78	6.54	5.52	4.66	13.6	20.08	19.54	55.72	14.56	25.82	36.16	14.18
Lu	1.22	0.86	0.82	2.3	1.76	1.96	1.64	1.52	3.92	6.12	5.46	15.52	2.5	4.24	5.56	2.74
Hf	1.52	1.02	1.02	1.82	3.02	3.96	3.62	2.36	6.08	10.98	7.4	31.98	2.7	6.72	10.76	3.4
Ta	0.196	0.15	0.19	0.52	0.28	0.36	0.4	0.28	0.5	0.84	0.94	3.28	0.2	0.64	1.24	0.26
Pb	3.14	3.32	5.02	7.36	7.66	7.58	11.16	31.66	18.4	20.28	27.9	59.3	6.86	5.28	12.2	3.76
Th	0.34	0.18	0.82	0.68	0.26	0.09	2.24	1.18	0.36	0.0156	0.03	0.6	0.46	0.022	1.22	0.086
U	0.178	0.02	0.22	0.048	0.0028	0.0034	0.026	0.008	0.0078	0.00198	0.0022	0.0096	0.044	0.0034	0.08	0.062

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Amostra local_spot Facies	MR-39c3-t2 b maciça	MR-39-1-6 inter maciça	MR02A AnC1P1b protomil	MR02A AnC3P2n protomil	MR02A AnC6P2n protomil	MR02A AnC7P2n protomil	MR03-1-1 n protomil	MR03-1-2 b protomil	MR03-1-3 b protomil	MR03-2-1 n protomil	MR03-3-t2 interm protomil	MR03-3-t3 n protomil	MR03-3-t5 b protomil	MR03-12-1 b protomil	MR03-12-2 interm protomil	MR03-12-3 n protomil	MR03-12-4 inter/n protomil
Li	579.14	110	768.02	836.28	458.43	755.98	5300.28	668.5	1093.99	3600.41	2452.87	6309.64	2104.57	3476.8	854.6	7026.3	9711.44
Be			3.25	4.83	3.92	4.46											
P			16.42	18.35	16.09	25.3											
Ca	25014.53	25014.54	0.29	0.75	0.75	0.75	7361.42	714.7	714.7	7361.42	4002.33	7361.42	714.7	2072.63	4931.44	5503.2	4931.44
Sc	15.83	19.72	1.222	1.56	1.611	1.55	9.82	1.602	1.722	9.76	3.87	7.73	2.24	2.35	1.777	5.03	6.09
Ti	15206.49	4654.31	6413.72	9983.29	5373.98	8854.5	16739.05	2693.22	3350.66	16067.44	8369.1	18100.54	4563.24	8490.26	4416.15	17496.53	21355.33
V	24.42	21.83	0.518	0.683	2.09	0.907	0.863	0.554	0.146	4.27	0.407	0.602	0.0988	0.116	1.126	0.368	0.333
Cr	12.69	3.47	2.82	3.39	3.1	4.29	5.38	0.68	6.77	<4.27	<2.34	<5.54	<1.79	<4.15	<1.29	<8.19	<10.90
Mn	<0.46	<0.108	3971.22	5235.11	2859.66	4885.85								22.3	<0.111	<0.72	102.76
Co	2.72	0.619	0.489	0.749	0.749	0.798	1.481	0.196	0.64	1.457	1.098	1.792	0.526	0.641	0.459	0.79	1.61
Ni	<2.93	1.39	0.042	0.129	0.21	0.135	<5.51	<0.78	<1.47	<4.83	<3.08	<6.45	<1.63	41.66	11.41	131.53	96.04
Cu	0.94	0.28	0.654	0.81	0.905	1.6	0.61	0.058	0.13	0.92	0.227	0.44	0.113	<0.28	<0.092	<0.54	<0.79
Zn	1732.77	433.42	1546.01	1994.54	1230.72	2182.49								3167.29	1152.1	7975.99	10130.01
Ga	12.01	3.29	2.16	4.36	4.28	4.25	14.32	2.155	5.79	21.29	6.84	15.07	2.94	7.09	3.54	15.65	18.55
Rb	27.96	3.87	13.34	18.27	12.3	19.9	44.65	5.17	27.9	27.09	20.92	50.49	23.3	34.34	5.12	63.69	94.72
Sr	40.81	104.07	8.6	13	6.82	13.75	20.39	2.72	<****	35.94	9.76	18.85	4.52	6.83	6.92	18.36	29.29
Y	218.26	214.01	18.21	35.81	16.5	83.32	94.29	6.97	68.13	222.48	51.46	104.8	48.61	20.27	26.95	60.94	101.51
Zr	646.6	4296.55	310.66	407.44	230.67	394.52	839.34	125.67	186.9	696.75	393.59	890.49	305.41	419.48	224.8	898.79	1119.86
Nb	214.59	39.5	17.65	26.82	21.28	25.89	74.78	9.79	25.52	69.16	29.37	59.51	16.74	28.06	14.75	77.84	106.99
Mo			0.104	0.173	0.201	0.442											
Sn	30.42	171.12	9.86	9.65	5.36	10.06	38.13	4.63	26.51	27.97	14.65	35.9	14.68	21.57	4.49	48.86	71.89
Sb			<0.023	0.047	<0.026	<0.051											
Cs	0.385	0.0353	0.0041	0.0529	0.296	0.442	0.335	0.00411	0.1238	0.0551	0.0114	0.03	0.0632	<0.052	<0.0167	<0.113	0.225
Ba	3.34	13.7	0.413	2.2	1.39	16.87	2.409	0.116	0.409	1.464	0.431	0.855	0.343	0.396	0.356	0.979	1.43
La	19.19	20.29	2.03	6.06	7.07	20.18	10.37	1.095	1.084	25.52	5	7.47	0.813	1.603	6.77	6.89	5.32
Ce	53.84	49.67	5.98	17.06	20.28	35.8	24.58	2.94	2.81	60.86	13.51	21.78	2.253	4.86	20.2	19.17	16.81
Pr	8.45	9.87	0.86	2.64	2.75	4.95	3.9	0.471	0.498	10.98	2.293	3.73	0.401	0.878	3.8	3.33	2.9
Nd	36.89	50.08	3.66	11.58	9.91	16.96	19.84	2.149	2.175	52.02	11.12	17.9	2.09	3.67	18.93	13.87	13.58
Sm	12.57	16.99	0.664	2.42	1.57	4.96	4.99	0.503	0.87	24.56	2.77	4.12	0.842	0.82	4.55	3.8	4.77
Eu	0.43	1.245	0.0266	0.074	0.077	0.115	0.172	0.0159	0.0333	0.589	0.0857	0.124	0.0464	<0.030	0.179	0.224	0.147
Gd	11.63	20.8	0.427	1.98	1.56	6.51	6.09	0.599	1.804	24.42	2.63	4.26	1.913	0.649	3.99	3.85	6.81
Tb	2.251	4.24	0.125	0.334	0.194	1.266	0.974	0.0847	0.394	3.35	0.467	0.791	0.475	0.171	0.518	0.675	1.515
Dy	21.96	37.94	1.77	3.63	2.08	9.03	8.25	0.797	3.74	23.14	4.26	8.64	4.37	2.06	3.82	7.15	15.13
Ho	7.55	9.17	0.807	1.386	0.792	2.18	2.78	0.2443	1.146	4.71	1.563	3.37	1.342	0.93	1.099	2.65	4.62
Er	42.1	43.04	5.3	9.25	4.94	9.14	15.6	1.685	4.72	18.11	9.06	19.33	5.92	6.29	5.54	14.79	22.1
Tm	11.61	10.28	1.564	2.62	1.67	2.32	4.62	0.496	0.985	3.63	2.71	5.64	1.42	2.041	1.667	4.86	6.45
Yb	118.51	93.28	19.09	32.37	19.37	25.31	57.91	7.08	10.12	43.87	32	65.78	15.3	26.09	20.31	55.9	68.37
Lu	22.04	15.46	4.5	7.39	4.49	5.85	14.02	1.973	2.453	11.2	7.67	15.76	3.54	6.22	4.88	13.58	16.36
Hf	23.92	155.54	9.66	12.32	6.08	10.68	26.28	3.99	6.85	35.4	12.71	29.54	10.04	13.66	7.57	28.77	36.22
Ta	2.98	0.456	0.2	0.45	0.441	0.949	1.15	0.1566	0.291	1.147	0.339	0.697	0.186	0.289	0.242	1.039	1.32
Pb	33.14	11.59	3.29	4.84	3.17	4.39	6.6	0.863	1.561	8.02	3.57	8.58	2.8	2.96	1.138	7.16	9.69
Th	1.281	16.23	<0.0041	0.0407	0.657	0.0236	0.347	0.0232	0.293	0.901	0.0702	0.217	0.1217	0.068	0.0419	0.034	0.062
U	0.0349	0.821	<0.0047	0.0623	0.153	0.342	1.315	0.0395	1.467	3.04	0.725	2.239	1.042	0.148	0.0067	0.189	0.17

Erro 2 sigma (2σ)

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR-39c3-t2	MR-39-1-6	MR02A	MR02A	MR02A	MR02A	MR03-1-1	MR03-1-2	MR03-1-3	MR03-2-1	MR03-3-t2	MR03-3-t3	MR03-3-t5	MR03-12-1	MR03-12-2	MR03-12-3	MR03-12-4
local_spot	b	inter	AnC1P1b	AnC3P2n	AnC6P2n	AnC7P2n	n	b	b	n	interm	n	b	b	interm	n	inter/n
Facies	maciça	maciça	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil
Li	54.56	10.36	106.88	116.96	66.92	116.56	552.76	71.02	88.86	381.22	214.56	552.72	200.44	351.04	76.98	685.64	995.3
Be	0	0	1.7	2.54	2.08	2.5	0	0	0	0	0	0	0	0	0	0	0
P	0	0	4.36	5.2	4.48	7.36	0	0	0	0	0	0	0	0	0	0	0
Ca	1669.18	1602.36	0.024	0.054	0.052	0.054	519.46	52.92	60.2	512.64	277.92	522.28	64.5	192.1	328.22	468.48	473.3
Sc	1.14	1.3	0.16	0.2	0.188	0.22	0.78	0.126	0.146	0.76	0.3	0.62	0.2	0.26	0.142	0.54	0.72
Ti	1009.06	300.14	993.14	1579.16	911.74	1625.38	1656.66	273.72	257.76	1639.84	570.24	1245.92	361.4	684.76	293.58	1336.22	1762.98
V	1.64	1.4	0.078	0.104	0.2	0.128	0.09	0.042	0.02	0.3	0.042	0.076	0.0176	0.052	0.09	0.114	0.142
Cr	5.16	1.46	0.82	1.08	0.8	1.2	4.02	0.56	3.94	3.58	1.96	4.62	1.5	3.52	1.1	7.02	9.32
Mn	0.62	0.148	353.86	456.08	257.22	466.6	0	0	0	0	0	0	0	1.86	0.172	1.26	8.6
Co	0.28	0.09	0.074	0.11	0.102	0.124	0.158	0.022	0.064	0.15	0.096	0.178	0.056	0.15	0.064	0.28	0.38
Ni	2.5	0.58	0.046	0.088	0.09	0.094	7.42	1.28	1.34	8.88	2.74	5.68	1.44	20.92	5.74	65.24	48.5
Cu	0.22	0.056	0.156	0.2	0.198	0.34	0.26	0.034	0.084	0.24	0.112	0.26	0.076	0.24	0.078	0.48	0.64
Zn	111.38	27.2	135.14	169.68	107.38	200.96	0	0	0	0	0	0	0	265.06	80.82	634.56	866.2
Ga	0.84	0.22	0.26	0.48	0.48	0.52	1.02	0.158	0.44	1.5	0.46	1.02	0.24	0.62	0.24	1.3	1.66
Rb	1.8	0.26	1.32	1.78	1.26	2.14	3.28	0.4	2.04	2.02	1.34	3.28	1.78	2.9	0.36	5.1	8.14
Sr	9.1	6.88	0.8	1.2	0.66	1.38	4.76	0.68	1.88	4.96	2.3	5.2	1.6	5.46	1.82	11.04	14.68
Y	14.16	13.46	1.66	3.2	1.52	8.02	6.42	0.48	5.18	15.02	3.44	7.06	3.8	1.66	1.8	4.7	8.42
Zr	42.34	270.4	28.44	36.52	21.32	38.56	61.4	9.46	14.14	51.3	26.28	60.12	23.86	43.54	20.9	90.28	117.86
Nb	13.84	2.5	1.46	2.14	1.72	2.18	5.16	0.7	1.94	4.76	1.96	4.04	1.32	2.3	1	6.02	8.92
Mo	0	0	0.058	0.1	0.084	0.158	0	0	0	0	0	0	0	0	0	0	0
Sn	2.14	10.48	1.12	1.12	0.66	1.3	3.32	0.42	1.98	2.52	0.98	2.44	1.14	2.58	0.52	5.62	8.5
Sb	0	0	0.024	0.036	0.028	0.046	0	0	0	0	0	0	0	0	0	0	0
Cs	0.048	0.0066	0.004	0.0154	0.042	0.066	0.044	0.00198	0.0138	0.0144	0.0062	0.0158	0.0084	0.044	0.0142	0.098	0.132
Ba	0.28	0.86	0.118	0.36	0.24	1.88	0.18	0.011	0.036	0.114	0.038	0.076	0.032	0.078	0.038	0.17	0.24
La	1.26	1.26	0.2	0.56	0.66	2	0.72	0.08	0.084	1.74	0.34	0.5	0.068	0.158	0.48	0.6	0.52
Ce	3.44	3.06	0.54	1.48	1.78	3.32	1.68	0.2	0.2	4.12	0.88	1.44	0.176	0.48	1.66	1.78	1.66
Pr	0.56	0.62	0.094	0.26	0.26	0.5	0.28	0.034	0.04	0.76	0.154	0.26	0.034	0.094	0.28	0.3	0.3
Nd	2.52	3.12	0.46	1.24	1.06	1.86	1.5	0.17	0.18	3.8	0.76	1.26	0.186	0.42	1.34	1.36	1.46
Sm	1.02	1.1	0.144	0.38	0.26	0.72	0.42	0.046	0.086	1.68	0.22	0.38	0.092	0.196	0.4	0.58	0.76
Eu	0.074	0.09	0.016	0.028	0.024	0.038	0.03	0.0034	0.0064	0.058	0.0144	0.026	0.0086	0.026	0.024	0.074	0.08
Gd	0.88	1.32	0.13	0.38	0.3	1.08	0.5	0.052	0.15	1.74	0.2	0.36	0.168	0.178	0.3	0.54	0.86
Tb	0.176	0.26	0.026	0.056	0.036	0.174	0.082	0.008	0.032	0.24	0.038	0.07	0.042	0.038	0.044	0.102	0.188
Dy	1.54	2.38	0.26	0.48	0.28	1.14	0.7	0.072	0.3	1.88	0.32	0.64	0.36	0.26	0.28	0.74	1.5
Ho	0.52	0.58	0.088	0.14	0.084	0.22	0.2	0.0192	0.088	0.32	0.112	0.24	0.108	0.1	0.082	0.26	0.44
Er	2.78	2.68	0.56	0.94	0.54	1.02	1.12	0.126	0.36	1.3	0.62	1.34	0.46	0.6	0.42	1.32	2.08
Tm	0.78	0.64	0.162	0.26	0.172	0.26	0.34	0.038	0.078	0.28	0.186	0.4	0.114	0.192	0.12	0.42	0.6
Yb	7.7	5.8	1.98	3.28	2.06	2.86	4.8	0.6	0.76	3.74	2.12	4.4	1.2	2.24	1.4	4.58	6
Lu	1.44	0.96	0.36	0.58	0.36	0.48	1.06	0.154	0.184	0.86	0.5	1.06	0.28	0.52	0.34	1.1	1.42
Hf	1.62	9.6	1.16	1.5	0.8	1.46	1.94	0.3	0.52	2.6	0.84	2	0.78	1.36	0.64	2.74	3.64
Ta	0.24	0.038	0.036	0.066	0.06	0.122	0.108	0.0148	0.03	0.106	0.034	0.074	0.022	0.06	0.03	0.162	0.22
Pb	2.18	0.74	0.28	0.4	0.26	0.38	0.62	0.082	0.116	0.76	0.24	0.58	0.22	0.32	0.106	0.72	1.02
Th	0.112	1.02	0.0034	0.017	0.076	0.0152	0.04	0.0034	0.028	0.078	0.0108	0.03	0.0144	0.022	0.01	0.022	0.04
U	0.0112	0.056	0.0028	0.0184	0.026	0.052	0.114	0.0044	0.108	0.26	0.052	0.158	0.082	0.034	0.003	0.048	0.05

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR03-12-5	MR21-1-1	MR38-4-2	MR38-4-3	MR38-4-4	MR38-4-5	MR38-4-6	MR27	MR27	MR01D	MR01D	MR01D	MR01D	MR01D
local_spot	b	n	inter/n	n	b	inter	n	AnC1P1b	AnC1P2n	AnC2P1b	AnC2P2n	n	b	n
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil	catacl	catacl	microgran	microgran	microgran	microgran	microgran
Li	9548.65	3615.09	388.71	413.81	179.78	555.5	807.07	433.12	1074.32	841.42	939.84	606.58	553.43	621.7
Be								3.19	8.67	9.81	9.17	5.66	5.85	5.6
P								5.53	9.82	11.82	14.78	11.88	10.62	8.76
Ca	2072.63	7004.07	4931.44	5503.2	2072.63	4931.44	5503.2	0.4	0.91	0.69	0.87	0.87	0.69	0.87
Sc	7.1	12.95	5.94	6.06	1.075	6.62	9.37	5.17	13.65	2	2.21	1.985	1.363	1.62
Ti	24924.43	26669.77	7175.7	7050.49	2641.51	9792.25	11023.84	1771.8	3812.96	4233.53	5230.82	4105.04	3232.78	3483.92
V	<0.140	2.34	6.4	8.06	0.899	7.18	11.43	2.439	6.44	0.461	0.505	0.521	0.321	0.382
Cr	18.32	<8.16	3	<1.45	0.76	3.48	3.62	0.82	1.61	2.06	2.85	1.48	2.1	1.74
Mn	<0.90		<0.14	<0.13	<0.064	<0.18	20.05	1586.74	3577.33	3149.94	4151.15	3200.95	2332.63	2732.16
Co	0.94	3.47	0.724	0.789	0.3	1.064	1.066	0.316	0.721	0.487	0.528	0.357	0.355	0.428
Ni	89.96	<8.66	18.96	17.81	7.98	21.55	30.3	0.042	0.11	0.063	0.105	0.06	<0.036	0.021
Cu	<0.73	0.79	0.181	0.198	0.066	0.243	0.455	0.338	1.29	0.577	0.79	0.37	0.471	0.61
Zn	10265.81		973.44	970.23	433.81	1181.51	1796.54	456.02	1073.72	1377.4	1532.8	1076.14	1032.96	1077.72
Ga	11.72	7.49	4.15	4.36	1.585	6.28	7.24	1.495	3.75	4	4.59	3.96	3.85	3.93
Rb	104.35	55.34	9.9	8.9	4.54	10.73	15.06	3.76	8.13	9.52	16.45	9.02	8.31	8.58
Sr	<16.02	25.52	9.5	11.28	3.2	23.39	15.14	5.33	13.81	3.64	4.61	3.81	2.57	3.59
Y	84.29	253.5	20.41	15.09	9.63	37.16	25.08	27.01	92.9	59.6	69.54	59.27	46.15	52.1
Zr	1485.68	1666.02	189.4	137.72	91.32	299.05	216.65	55.91	108.2	246	329.3	237.58	190.63	194.02
Nb	129.27	309.63	27.64	25	12.36	33.61	44.54	10.99	23.41	27.8	34.72	21.67	23.15	18.92
Mo								0.11	0.283	0.085	0.176	0.135	0.071	0.179
Sn	70.58	40.57	6.5	5.84	2.69	9.08	12.16	2.28	6.08	7.45	8.33	4.98	4.84	4.16
Sb								0.0118	0.047	0.039	<0.026	<0.023	0.042	0.035
Cs	<0.140	<0.032	<0.0207	0.0241	<0.0091	0.067	<0.035	0.1154	0.232	0.126	0.476	0.0994	0.206	0.182
Ba	0.96	1.746	0.896	1.192	0.1936	1.994	5.98	0.821	1.68	1.55	0.81	0.94	1.38	1.88
La	3.98	9.09	4.59	6.74	2.024	4.62	5.74	3.05	6.82	4.99	6.25	5.6	3.69	5.27
Ce	11.26	24.49	13.47	15.94	5.84	13.03	14.9	8.36	17.83	13.87	17.8	16.13	11.26	14.6
Pr	1.62	3.53	1.952	2.228	0.79	1.808	1.984	1.477	3.09	2.23	2.83	2.59	1.86	2.35
Nd	5.42	13.61	7.06	8.05	2.84	6.92	6.97	7.27	16.22	10.18	12.27	11.9	9.08	12.49
Sm	1.34	3.34	1.063	1.197	0.422	1.708	1.046	2.5	5.35	3.11	4.28	3.47	3.09	3.73
Eu	<0.067	0.096	0.028	0.0378	0.0167	0.105	0.0349	0.124	0.262	0.111	0.145	0.14	0.149	0.177
Gd	1.83	5.16	0.637	0.823	0.322	2.31	0.68	2.87	7.59	3.95	4.62	4.67	5.06	4.99
Tb	0.462	1.342	0.159	0.183	0.0751	0.482	0.149	0.483	1.392	0.858	1.108	0.892	1.036	0.972
Dy	6.08	22.22	2.42	2.165	1.034	5.3	2.41	3.55	9.74	7.42	9.89	8.03	8.49	7.91
Ho	2.83	11.08	1.072	0.852	0.467	1.595	1.244	0.865	2.309	2.42	2.75	2.37	2.11	1.94
Er	16.85	71.86	7.23	5.44	2.99	7.78	7.91	3.39	8.68	11.2	13.63	9.68	8.31	8.06
Tm	5.3	21.79	2.016	1.585	0.846	2.294	2.322	0.823	2.003	2.88	3.4	2.32	2.09	1.93
Yb	69.33	237.24	23.84	18.89	9.33	24.69	26.77	8.95	21.31	31.25	34.97	23.75	21.01	21.74
Lu	16.39	49	5.07	3.95	1.841	5.47	5.56	1.998	4.93	6.13	7.28	5.19	4.75	4.78
Hf	46.4	40.15	4.53	3.2	2.534	7.44	5.64	1.419	3.02	6.68	9	6.62	5.75	5.66
Ta	2.77	3.05	0.674	0.414	0.211	0.705	0.609	0.1163	0.238	0.34	0.857	0.299	0.539	0.324
Pb	7.24	40.27	12.51	4.62	1.971	5.54	8.41	2.786	6.62	10.65	15.18	7.4	8.71	19.49
Th	0.142	0.0297	0.704	0.347	0.0481	7.18	0.312	1.095	3.18	0.595	2.117	0.448	2.264	0.783
U	1.97	0.0216	0.449	0.257	0.0495	0.634	0.29	0.0943	0.138	0.087	0.234	0.0527	0.188	0.1

Erro 2 sigma (2σ)

Tabela 8: Análises químicas de elementos-traços por LA-ICP-MS de cristais de anfibólios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR03-12-5	MR21-1-1	MR38-4-2	MR38-4-3	MR38-4-4	MR38-4-5	MR38-4-6	MR27	MR27	MR01D	MR01D	MR01D	MR01D	MR01D
local_spot	b	n	inter/n	n	b	inter	n	AnC1P1b	AnC1P2n	AnC2P1b	AnC2P2n	n	b	n
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil	catacl	catacl	microgran	microgran	microgran	microgran	microgran
Li	1217.1	308.26	46.26	49.3	21.42	66.36	96.7	50.8	125.96	208.02	242.4	163.56	156.54	193.7
Be	0	0	0	0	0	0	0	1.68	4.52	5.36	5.02	3.1	3.22	3.22
P	0	0	0	0	0	0	0	1.06	2.12	2.78	3.22	2.36	2.24	2.18
Ca	298.18	532.14	331.16	371.68	139.74	338.48	384.7	0.026	0.06	0.05	0.06	0.058	0.046	0.058
Sc	0.94	1.04	0.44	0.46	0.086	0.5	0.72	0.38	1.02	0.24	0.26	0.192	0.148	0.182
Ti	2792.86	1893.24	487.3	480.22	179.76	672.22	763.86	134.62	289.68	1201.42	1567.72	1301.92	1087.88	1320.46
V	0.12	0.2	0.52	0.66	0.076	0.58	0.94	0.19	0.5	0.09	0.092	0.072	0.054	0.066
Cr	8.98	6.76	1.42	1.36	0.62	1.8	2.52	0.28	0.62	0.82	0.88	0.56	0.56	0.58
Mn	2.28	0	0.26	0.26	0.12	0.34	1.56	116.66	262.96	241.56	317.04	243.52	181.54	221.54
Co	0.34	0.32	0.078	0.084	0.034	0.108	0.128	0.038	0.084	0.102	0.104	0.066	0.066	0.086
Ni	45.9	7.6	45.44	42.68	19.12	51.64	72.64	0.028	0.064	0.076	0.102	0.05	0.04	0.03
Cu	0.6	0.36	0.106	0.104	0.044	0.13	0.188	0.066	0.2	0.192	0.22	0.104	0.122	0.154
Zn	1172.94	0	76.54	76.46	34.16	93.68	143.42	37.86	89.14	141.54	160.86	115.62	115.38	130.16
Ga	1.42	0.56	0.28	0.3	0.112	0.44	0.52	0.126	0.3	0.42	0.44	0.36	0.34	0.38
Rb	11.96	3.78	0.7	0.62	0.32	0.76	1.08	0.34	0.74	0.8	1.34	0.72	0.68	0.74
Sr	13.56	8.22	2.14	2.14	0.92	3.04	3.78	0.38	0.98	0.34	0.42	0.34	0.24	0.36
Y	9.48	17.82	1.54	1.14	0.72	2.82	1.92	1.86	6.4	5.14	6.02	5.16	4.14	4.96
Zr	192.5	117.26	13.44	9.84	6.48	21.4	15.72	4.24	8.2	21.58	29.12	21.22	17.56	19
Nb	14.54	21.76	1.86	1.68	0.82	2.28	3.04	0.9	1.94	2.52	3.14	1.98	2.18	1.9
Mo	0	0	0	0	0	0	0	0.04	0.092	0.078	0.104	0.068	0.048	0.088
Sn	9.9	2.96	0.62	0.56	0.26	0.84	1.14	0.24	0.6	0.96	1.06	0.64	0.66	0.62
Sb	0	0	0	0	0	0	0	0.011	0.026	0.038	0.032	0.022	0.026	0.026
Cs	0.118	0.028	0.0176	0.018	0.0076	0.026	0.03	0.0138	0.028	0.028	0.056	0.0162	0.024	0.026
Ba	0.2	0.152	0.072	0.094	0.0192	0.148	0.42	0.11	0.24	0.36	0.24	0.22	0.3	0.42
La	0.5	0.66	0.32	0.46	0.138	0.32	0.4	0.22	0.5	0.58	0.74	0.66	0.46	0.7
Ce	1.42	1.68	0.88	1.04	0.38	0.86	1	0.6	1.28	1.24	1.58	1.44	1.04	1.44
Pr	0.22	0.26	0.136	0.156	0.056	0.132	0.148	0.112	0.24	0.24	0.3	0.28	0.2	0.28
Nd	0.84	1.08	0.52	0.6	0.2	0.52	0.56	0.64	1.42	1.18	1.34	1.2	0.98	1.42
Sm	0.42	0.38	0.13	0.148	0.052	0.192	0.176	0.22	0.5	0.52	0.64	0.48	0.44	0.58
Eu	0.064	0.032	0.0136	0.0148	0.006	0.024	0.0182	0.02	0.044	0.042	0.046	0.034	0.036	0.048
Gd	0.46	0.48	0.09	0.108	0.042	0.22	0.13	0.32	0.84	0.76	0.84	0.8	0.9	0.98
Tb	0.1	0.12	0.02	0.024	0.0094	0.046	0.026	0.042	0.116	0.108	0.126	0.094	0.108	0.112
Dy	0.86	1.64	0.2	0.192	0.086	0.4	0.24	0.32	0.88	1	1.3	1.06	1.16	1.18
Ho	0.36	0.8	0.086	0.072	0.038	0.126	0.106	0.076	0.198	0.26	0.3	0.24	0.22	0.24
Er	2.06	5	0.54	0.42	0.22	0.6	0.62	0.3	0.76	1	1.18	0.8	0.72	0.74
Tm	0.64	1.52	0.148	0.122	0.062	0.172	0.182	0.07	0.168	0.3	0.34	0.24	0.22	0.22
Yb	8.02	16.32	1.64	1.32	0.64	1.74	1.92	0.86	2.02	3.42	3.84	2.64	2.42	2.72
Lu	1.88	3.38	0.36	0.3	0.134	0.4	0.42	0.158	0.38	0.62	0.72	0.52	0.48	0.52
Hf	5.8	2.84	0.34	0.26	0.186	0.54	0.44	0.172	0.38	0.92	1.18	0.84	0.78	0.84
Ta	0.38	0.26	0.064	0.048	0.022	0.072	0.072	0.0174	0.036	0.062	0.102	0.04	0.06	0.048
Pb	0.96	2.74	0.84	0.36	0.146	0.42	0.64	0.194	0.46	1.1	1.54	0.76	0.94	2.22
Th	0.05	0.0124	0.07	0.042	0.0078	0.6	0.044	0.084	0.24	0.084	0.192	0.05	0.178	0.084
U	0.38	0.0086	0.04	0.028	0.0064	0.056	0.034	0.0134	0.024	0.026	0.044	0.0136	0.03	0.024

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR-39-1-3	MR-39c1-1	MR-39c1-2	MR-39c1-3	MR-39c1-4	MR-39c2-1	MR-39c2-2	MR-39c2-3	MR-39-4-1	MR-39-4-2	MR-39c2-t1	MR-39-1-1 80um	MR02A	MR02A	MR02A	MR03-4-2
Local_spot	b	b/inter	b	inter/b	n	mantle xt1	mantle xt2	mantle xt3	mantle n	mantle b	mantle	b	NPYc1P1b	NPYc1P2n	PyC6P2n	n
Facies	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	protomil	protomil	protomil	protomil
Li	4.4	9.52	12.22	16.53	9.6	6.94	4.92	6.78	3.07	21.46	3.94	3.55	1.64	4.44	4.61	5.55
Be													1.64	<1.42	<0.47	
P													40.15	91.29	30.89	
Ca	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	3502.03	0.41	0.61	0.61	1715.28
Sc	2.041	1.24	1.59	1.72	1.4	3.07	3.4	3.2	2.46	4.41	2.95	1.996	2.69	5.93	2.26	1.436
Ti	365.32	5084.54	7707.22	8367.19	4249.69	945.67	918.57	842.45	693.88	11689.54	706.8	329.29	12229.07	14493.06	6961.04	1659.03
V	2.194	2.28	3.53	8.79	2.25	7.89	9.26	6.26	3.19	4.09	10.32	2.113	1.313	1.33	0.716	0.0683
Cr	0.393	<1.17	<1.70	<2.38	1.63	<1.11	2.29	<0.88	0.5	<3.81	<1.04	0.321	5.83	15.51	3.58	<0.66
Mn	8.56	649.91	756.17	703.3	609.43	212.23	183.01	240.95	227.87	704.53	198.14	<0.0097	2458.66	6788.33	1092.79	
Co	0.0356	0.225	0.265	0.422	0.229	0.162	0.162	0.222	0.149	0.211	0.13	<0.0104	0.681	2.42	0.342	0.188
Ni	0.064	<0.57	<0.80	<1.16	<0.52	<0.56	<0.56	<0.44	<0.213	<2.04	<0.51	<0.060	<0.119	<0.24	0.088	<0.66
Cu	0.0174	0.545	1.24	2.18	3.32	0.262	0.195	0.2	0.0219	1.19	0.098	0.0097	1.1	3.19	0.76	0.071
Zn	29.95	52.87	71.11	95.77	52.73	33.52	33.58	32.38	35.47	123.82	32.52	28.48	1691.44	8551.95	386.69	
Ga	0.2538	1.3	2.02	3.28	1.44	2.27	2.12	1.7	0.685	9.86	1.96	0.2204	15.33	25.22	5.27	1.786
Rb	0.00808	1.429	0.225	0.324	10.12	1.81	1.047	1.94	0.0653	7.01	0.0398	0.00794	0.023	0.07	0.166	0.0255
Sr	2.28	4.38	10.65	8.94	5.72	3.59	0.945	1.88	1.5	3.145	0.84	2.67	2.86	8.72	2.12	2.04
Y	27.98	26.67	53.68	15.19	26.79	2.15	3.6	1.96	8.5	216.16	3.31	27.31	35.79	26.9	7.5	45.57
Zr	521.41	453.75	629.67	446.27	631.91	262.64	380.85	257.11	451.37	570.25	186.87	534.48	248.95	517.72	262.28	349.08
Nb	0.1851	2.41	9.34	5.52	6.33	2.47	0.198	0.732	0.0209	94.2	0.0304	0.0933	282.54	882.38	124.68	234.27
Mo													0.87	2.18	0.453	
Sn	27.03	72.16	129.32	106.59	109.88	94.69	109.43	37.81	45.77	106.96	115.48	20.32	194.79	49.51	27.52	17.45
Sb													0.095	<0.209	<0.065	
Cs	0.0005	0.482	0.0263	0.134	0.86	0.66	0.175	0.93	0.0408	1.85	0.007	<0.00046	<0.01	<0.031	0.0383	0.01
Ba	0.133	2.71	2.59	2.78	3.08	1.53	0.736	2.57	0.15	47.52	0.077	0.0656	1.02	0.8	2.4	0.354
La	2.895	2.51	3.65	2.17	2.88	1.78	0.421	1.08	0.528	31.47	0.1006	3.25	27.4	29.28	8.89	16.46
Ce	9.41	3.97	6.71	2.54	3.59	1.42	1.01	1.58	3.17	29.47	0.429	10.52	45.7	50.43	23.61	49.16
Pr	1.497	0.459	0.881	0.324	0.499	0.392	0.229	0.258	0.854	8.27	0.1314	1.678	4.87	5.2	3.08	7.77
Nd	7.16	1.751	3.73	1.23	1.95	1.689	1.143	1.116	4.83	42.09	0.76	7.56	15.57	17.96	11.47	34.21
Sm	2.243	0.389	0.81	0.339	0.374	0.417	0.561	0.255	2.01	22.76	0.503	2.179	2.16	2.6	1.95	7.15
Eu	0.1186	0.0576	0.131	0.061	0.0523	0.0106	0.0316	<0.0065	0.083	1.75	0.0239	0.1215	0.058	0.062	0.061	0.185
Gd	2.862	0.65	1.7	0.53	0.65	0.352	0.55	0.201	2.13	39.63	0.564	2.791	2.29	2.02	1.42	4.13
Tb	0.54	0.134	0.352	0.124	0.14	0.0619	0.095	0.0417	0.383	9.08	0.1014	0.522	0.21	0.148	0.191	0.602
Dy	4.5	1.59	3.66	1.32	1.52	0.4	0.641	0.308	2.71	70.17	0.62	4.31	3.39	2.42	1.12	4.68
Ho	1.098	0.579	1.129	0.341	0.496	0.0816	0.141	0.0739	0.523	12.69	0.1357	1.006	1.697	1.26	0.326	1.31
Er	4.43	3.1	6.15	1.86	3.36	0.361	0.64	0.358	2.23	42.76	0.632	4	10.67	10.83	2.16	6
Tm	1.012	1.48	2.39	0.82	1.97	0.194	0.278	0.15	0.61	6.88	0.299	0.946	2.88	3.7	0.985	1.407
Yb	9.47	31.39	43.21	16.47	43.17	4.36	6.16	3.1	7.01	74.58	7.09	9.25	33.03	50.26	16.56	14.52
Lu	1.614	8.49	10.89	4.69	11.8	1.53	2	0.931	1.51	18.15	2.068	1.558	6.77	10.4	4.64	2.86
Hf	22.46	26.2	38.14	80.86	35.52	21.39	23.66	16.04	11.37	27.98	17.2	15.17	7.71	12.86	6.62	6.44
Ta	0.00676	0.435	0.739	0.756	0.437	0.0484	0.0139	0.069	0.0068	2.05	0.0017	0.00414	4.36	5.79	2.18	10.24
Pb	0.386	0.657	1.24	2.04	1.6	0.982	0.154	1.007	0.0852	20.05	0.0576	0.301	0.515	0.453	0.586	1.385
Th	0.0432	3.91	2.43	2.33	1.72	0.619	0.0284	1.64	0.0051	10.53	0.0206	0.02154	0.546	0.595	0.052	0.794
U	0.00102	0.0353	0.0666	0.129	0.0477	0.0389	0.00459	0.0551	0.00152	0.361	<0.00074	0.00127	0.477	0.949	0.292	0.566

protomil = protomilonítica; catac= cataclástica; microgran = microgranítica. b = borda; n = núcleo; inter = zona intermediária

Erro 2 sigma (2σ)

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR-39-1-3	MR-39c1-1	MR-39c1-2	MR-39c1-3	MR-39c1-4	MR-39c2-1	MR-39c2-2	MR-39c2-3	MR-39-4-1	MR-39-4-2	MR-39c2-t1	MR-39-1-1 80um	MR02A	MR02A	MR02A	MR03-4-2
Local_spot	b	b/inter	b	inter/b	n	mantle xt1	mantle xt2	mantle xt3	mantle n	mantle b	mantle	b	NPYc1P1b	NPYc1P2n	PyC6P2n	n
Facies	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	maciça	protomil	protomil	protomil	protomil
Li	0.42	2.9	3.8	5.3	3.16	2.36	1.74	2.5	1.3	9.52	0.42	0.32	0.5	1.28	0.86	0.68
Be	0	0	0	0	0	0	0	0	0	0	0	0	1.2	1.06	0.44	0
P	0	0	0	0	0	0	0	0	0	0	0	0	10	23.58	7.68	0
Ca	223.34	240.4	256.54	269.12	240.02	239.04	238.9	234.84	227.06	295.02	243.38	223.34	0.04	0.074	0.046	116.2
Sc	0.134	0.26	0.36	0.4	0.32	0.74	0.86	0.84	0.74	1.4	0.22	0.13	0.38	0.92	0.28	0.114
Ti	23.46	1126.08	1746.02	1948.9	1014.86	233.86	236	225.34	211.48	3752.88	48.18	21.12	1687.12	2163.18	979.42	196.72
V	0.14	0.28	0.44	1.14	0.3	1.04	1.26	0.88	0.5	0.7	0.7	0.134	0.2	0.32	0.122	0.0092
Cr	0.138	0.98	1.52	2.1	0.94	0.96	0.98	0.76	0.34	3.28	0.98	0.134	1.86	4.56	1.26	0.56
Mn	0.54	66.46	79.78	76.58	66.24	23.72	21.1	28.64	30.26	101.18	13.36	0.0136	223.76	711.24	91.74	0
Co	0.0078	0.046	0.068	0.096	0.046	0.042	0.042	0.04	0.024	0.13	0.036	0.0086	0.126	0.4	0.074	0.02
Ni	0.052	0.48	0.72	1.04	0.46	0.48	0.48	0.38	0.192	1.76	0.48	0.052	0.14	0.28	0.104	1.08
Cu	0.0046	0.134	0.3	0.52	0.78	0.078	0.062	0.062	0.0126	0.4	0.036	0.004	0.3	0.82	0.22	0.034
Zn	1.88	8.66	11.92	16.48	9.2	6.04	6.26	6.24	7.66	28.32	2.22	1.78	153.28	891.22	32.4	0
Ga	0.0176	0.24	0.4	0.64	0.28	0.46	0.46	0.38	0.172	2.6	0.148	0.0156	1.6	3	0.56	0.132
Rb	0.00162	0.19	0.04	0.058	1.38	0.26	0.154	0.28	0.0122	1.22	0.013	0.0016	0.024	0.058	0.042	0.0064
Sr	0.24	2.38	4.66	4.98	2.68	2.14	1.72	1.48	0.88	6.06	1.58	0.26	0.32	1.04	0.22	0.68
Y	1.76	3.02	6.26	1.84	3.22	0.28	0.46	0.26	1.24	34.1	0.24	1.72	3.36	2.96	0.68	3.06
Zr	32.66	81.16	115.76	84.72	122.9	53.02	80.1	56.44	113.94	152.78	12.46	33.42	23.3	55.44	22.72	27
Nb	0.0126	0.36	1.44	0.88	1.02	0.42	0.038	0.134	0.0054	20.32	0.0082	0.0068	24.48	88.8	9.72	16.16
Mo	0	0	0	0	0	0	0	0	0	0	0	0	0.28	0.7	0.176	0
Sn	1.66	6.1	11.28	9.58	9.62	8.42	9.94	3.5	4.54	11.72	7.42	1.24	20.32	6.1	2.86	1.76
Sb	0	0	0	0	0	0	0	0	0	0	0	0	0.094	0.16	0.056	0
Cs	0.00032	0.144	0.0108	0.046	0.28	0.22	0.062	0.34	0.0176	0.82	0.0038	0.0004		0.03	0.015	0.0026
Ba	0.01	0.48	0.48	0.52	0.58	0.3	0.154	0.54	0.038	11.96	0.026	0.0064	0.28	0.36	0.42	0.026
La	0.18	0.48	0.72	0.44	0.6	0.38	0.096	0.26	0.142	8.9	0.0152	0.2	2.6	3.22	0.8	1.14
Ce	0.58	1.02	1.76	0.7	1	0.42	0.3	0.5	1.14	11.24	0.036	0.64	4.18	5.34	2	3.38
Pr	0.092	0.068	0.132	0.054	0.078	0.064	0.04	0.044	0.162	1.68	0.015	0.104	0.5	0.64	0.3	0.54
Nd	0.44	0.19	0.4	0.178	0.22	0.194	0.142	0.136	0.58	5.5	0.086	0.46	1.78	2.56	1.26	2.6
Sm	0.142	0.106	0.22	0.116	0.112	0.126	0.172	0.084	0.7	8.4	0.072	0.138	0.42	0.68	0.36	0.48
Eu	0.0084	0.017	0.036	0.026	0.0162	0.0084	0.0118	0.0062	0.026	0.58	0.0094	0.0086	0.036	0.052	0.03	0.0156
Gd	0.178	0.22	0.6	0.22	0.24	0.144	0.22	0.09	1.04	20.28	0.072	0.174	0.5	0.68	0.34	0.3
Tb	0.034	0.028	0.076	0.032	0.032	0.0162	0.024	0.0116	0.104	2.6	0.0142	0.032	0.05	0.06	0.042	0.042
Dy	0.28	0.32	0.74	0.28	0.32	0.094	0.15	0.078	0.72	19.56	0.07	0.26	0.5	0.56	0.22	0.42
Ho	0.068	0.098	0.194	0.066	0.09	0.0172	0.028	0.016	0.114	2.94	0.0162	0.062	0.198	0.22	0.058	0.088
Er	0.28	0.94	1.9	0.6	1.1	0.126	0.22	0.136	0.96	19.34	0.064	0.24	1.16	1.46	0.3	0.44
Tm	0.064	0.44	0.72	0.26	0.62	0.066	0.098	0.054	0.26	2.98	0.028	0.06	0.32	0.48	0.12	0.108
Yb	0.58	6.08	8.56	3.38	8.96	0.94	1.38	0.72	1.84	20.6	0.5	0.58	3.5	6.14	1.74	1.38
Lu	0.1	1.46	1.92	0.86	2.18	0.3	0.4	0.192	0.34	4.42	0.144	0.096	0.62	1.12	0.38	0.24
Hf	1.38	6.1	9.08	19.8	8.94	5.58	6.4	4.52	3.66	9.5	1.14	0.94	1.08	2.06	0.88	0.5
Ta	0.00114	0.072	0.126	0.134	0.076	0.0124	0.0058	0.0154	0.0026	0.46	0.003	0.00092	0.46	0.72	0.22	0.78
Pb	0.026	0.112	0.22	0.36	0.28	0.178	0.034	0.192	0.02	4.44	0.016	0.02	0.102	0.144	0.096	0.154
Th	0.0034	0.9	0.58	0.58	0.44	0.164	0.0092	0.48	0.002	3.7	0.005	0.002	0.092	0.14	0.022	0.058
U	0.0003	0.0084	0.0158	0.03	0.0112	0.0096	0.00198	0.0136	0.0007	0.104	0.00096	0.00032	0.078	0.17	0.05	0.054

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR03-5-2	MR43-1-1	MR43-1-3	MR43-1-4	MR03-12-1b	MR03-12-2n	MR03-13-1b	MR03-13-2n	MR38-3-1	MR38-3-2	MR38-3-3	MR38-3-4	MR27	MR27	MR27	MR27
Local_spot	b	n	n	b	b	n	b	n	b	inter	n	b	PyC2P1n	PyC2P1n-1	PyC2P2b	PyC2P3b
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	catác	catác	catác	catác
Li	2.29	0.76	0.72	<0.155	2.27	9.48	13.62	27.52	<1.17	<1.41	<0.93	<0.82	8.63	2.39	16.07	4.05
Be													1.8	1.35	3.51	1.95
P													4.96	1.72	12.36	3.98
Ca	1286.46	2001.16	2001.16	857.64	1286.46	1715.28	1286.46	1715.28	2787.33	3502.03	3573.5	2787.33	0.46	0.46	0.3	0.3
Sc	4.18	3.14	1.894	1.144	6.41	4.79	7.24	5.67	11.22	19.03	18.07	9.57	1.509	0.481	4.06	1.152
Ti	854.35	10988.96	5017.75	2597.03	3866.75	5562.4	6616.18	8294.08	12167.6	26911.82	15779.74	12185.75	802.47	421.53	2024.18	569.31
V	<0.025	0.539	0.501	0.328	0.0451	0.102	0.155	0.113	0.789	2.98	4.14	7.39	0.812	0.344	2.154	0.518
Cr	4.44	8.37	2.86	1.18	<1.25	<2.15	<1.49	2.72	<4.04	9.59	<3.33	4.63	0.73	0.282	2.1	0.545
Mn					267.53	338.3	<0.12	600.52	1033.18	1274.8	1151.14	1169.83	88.21	14.1	227.85	37.56
Co	<0.054	0.384	0.175	0.33	<0.039	<0.066	0.263	0.274	0.183	0.192	0.388	0.473	0.0172	0.0049	0.0513	0.0103
Ni	<2.37	<3.08	<1.21	<0.63	28.07	69.48	65.52	80.74	52.53	78.17	26.58	28.39	<0.02	0.0161	0.088	0.0166
Cu	0.134	0.491	0.119	0.051	3.06	<0.135	<0.095	<0.161	<0.30	0.36	<0.24	<0.205	0.176	0.103	0.148	0.082
Zn					274.49	564.34	723.83	651.12	195.78	226.73	188.66	209.37	20.65	2.26	33.02	5.04
Ga	13.22	10.14	4.56	2.102	3.08	6.85	4.37	4.76	8.68	9.49	6.7	5.51	2.105	0.522	3.81	1.527
Rb	0.066	0.0155	0.0084	0.0176	0.015	0.086	0.412	0.0315	0.044	0.0555	0.0385	0.035	0.1131	0.876	1.677	0.0928
Sr	1.455	13.1	4.37	2.7	5.73	9.34	3.6	1.81	3.605	12.48	2.94	2.545	4.61	10.74	1.956	3.27
Y	1.064	7.63	22.48	17.55	14.64	26.53	9.57	19.69	3.23	3.75	1.497	0.607	45.64	96.76	25.66	34.94
Zr	717.54	599.13	168.54	63.08	2794.58	1789.88	2955.07	2281.42	4652.48	7561.98	6919.52	1541.96	98.38	22.64	312.3	42.38
Nb	0.00895	404.41	50.01	84.02	207.61	713.54	648.13	457.77	1884.98	1882.17	844.52	248.44	2.6	0.789	2.66	2.068
Mo													0.0195	<0.0041	0.045	<0.0141
Sn	0.42	62.22	51.33	7.28	25.97	93.36	24.33	20.57	102.02	96.29	104.75	232.96	19.14	2.99	37.1	14.81
Sb													0.0071	0.0087	<0.021	0.0148
Cs	0.0401	<0.0095	0.0065	0.0092	0.0268	0.106	0.112	<0.033	<0.050	<0.058	<0.042	<0.035	0.0101	0.2217	0.465	0.0126
Ba	0.149	0.607	3.29	0.0822	1.364	2.64	0.038	0.191	<0.077	0.284	0.514	0.054	0.435	0.53	2.51	0.739
La	1.594	11.59	16.98	5.65	18.18	26.56	1.557	3.6	3.25	3.92	5.85	1.219	1.671	0.889	0.962	0.933
Ce	4.32	20.03	21.1	9.9	53.6	75.4	5.62	11.07	8.68	9.66	16.77	4.68	3.98	2.126	2.81	2.507
Pr	0.633	2.632	2.166	1.074	7.81	10.31	1.052	1.944	1.449	1.548	2.69	0.931	0.862	0.401	0.603	0.42
Nd	2.57	8.59	7.59	3.74	32.21	41.05	5.1	8.92	5.11	5.23	9.84	3.95	5.56	2.65	4.2	2.48
Sm	0.428	0.924	1.127	0.537	7.82	7.62	1.309	2.56	0.815	1.02	1.095	0.731	2.97	1.591	2.32	1.272
Eu	0.0129	0.0175	0.0403	0.012	0.33	0.231	0.0371	0.059	0.046	<0.038	<0.024	<0.024	0.128	0.1054	0.147	0.0602
Gd	0.169	0.566	1.119	0.41	3.54	3.63	0.77	1.395	0.308	0.23	0.298	0.192	4.6	4.71	2.68	2.3
Tb	0.0269	0.089	0.1816	0.0674	0.421	0.51	0.129	0.219	<0.036	<0.042	0.04	<0.0206	0.793	1.129	0.73	0.488
Dy	0.161	0.827	2.421	1.288	2.65	3.97	1.076	2.02	0.301	0.337	0.247	0.057	5.47	8.36	5.09	3.2
Ho	0.0471	0.329	1.136	0.783	0.717	1.192	0.384	0.579	0.173	0.176	0.065	0.033	1.042	1.707	0.89	0.557
Er	0.382	2.68	7.1	5.84	4.06	7.14	2.84	3.71	1.22	1.34	0.321	0.339	3.07	4.05	3.22	1.445
Tm	0.15	0.97	1.937	1.591	1.282	2.053	1.095	1.228	0.358	0.705	0.124	0.183	0.537	0.469	0.873	0.209
Yb	2.32	13.31	18.69	14.76	17.14	23.14	16.05	17.07	4.82	9.1	1.7	5.07	5.42	2.86	11.87	1.838
Lu	0.622	3.05	3.1	2.496	3.91	4.58	4	4.44	1.03	2.81	0.53	1.91	1.081	0.377	3.04	0.476
Hf	12.61	10.96	4.67	1.361	42.65	30.46	50.51	43.74	88.8	157.87	137.3	28.91	4.63	2.82	18.97	4.7
Ta	278.28	26.18	1.683	0.657	109.03	40.38	55.96	50	24.73	23.92	49.15	12.03	0.0434	0.0416	0.13	0.0512
Pb	0.161	0.798	0.566	0.019	0.404	3.2	0.091	1.545	0.092	0.987	0.533	<0.043	0.512	0.262	0.659	0.281
Th	0.0634	1.686	1.367	0.0114	0.169	0.291	0.0204	0.3	0.0056	0.0373	0.077	<0.0054	1.27	0.377	0.462	0.419
U	0.0412	0.0496	0.767	0.0239	0.0925	0.403	0.0358	0.533	0.0097	0.205	0.279	0.0023	0.166	0.0344	0.0445	0.0347

Erro 2 sigma (2σ)

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR03-5-2	MR43-1-1	MR43-1-3	MR43-1-4	MR03-12-1b	MR03-12-2n	MR03-13-1b	MR03-13-2n	MR38-3-1	MR38-3-2	MR38-3-3	MR38-3-4	MR27	MR27	MR27	MR27
Local_spot	b	n	n	b	b	n	b	n	b	inter	n	b	PyC2P1n	PyC2P1n-1	PyC2P2b	PyC2P3b
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	catác	catác	catác	catác
Li	0.82	0.34	0.22	0.134	0.48	1.48	1.96	3.94	0.98	1.2	0.8	0.7	1.08	0.32	2.06	0.52
Be	0	0	0	0	0	0	0	0	0	0	0	0	0.98	0.7	1.92	1.04
P	0	0	0	0	0	0	0	0	0	0	0	0	0.94	0.32	2.24	0.74
Ca	112.36	147.6	139.9	63.02	97.28	137.02	101.58	142.22	233.54	293.32	270.48	214.52	0.03	0.03	0.022	0.02
Sc	0.38	0.24	0.146	0.092	0.48	0.38	0.54	0.46	1.02	1.7	1.52	0.82	0.126	0.042	0.34	0.096
Ti	114.34	785.28	344.46	182.16	328.72	483.66	572.36	732.74	2118.62	4685.38	2718.02	2102.4	60.84	31.68	160.94	43.28
V	0.022	0.05	0.04	0.026	0.0138	0.026	0.024	0.03	0.104	0.3	0.38	0.66	0.072	0.03	0.192	0.048
Cr	2.24	2.88	1.24	0.7	1.06	1.84	1.28	2.16	3.4	4.34	2.84	2.56	0.24	0.078	0.58	0.19
Mn	0	0	0	0	25.9	33.34	0.28	59.9	86.44	106.64	91.76	93.96	6.46	1.02	17.58	2.76
Co	0.046	0.054	0.028	0.03	0.032	0.054	0.05	0.074	0.134	0.16	0.114	0.104	0.0072	0.0026	0.0182	0.0048
Ni	3.98	3.04	1.08	0.56	92.46	228.8	215.72	265.88	20.98	30.94	11.12	11.58	#VALOR!	0.0104	0.058	0.0126
Cu	0.112	0.124	0.06	0.034	0.4	0.114	0.082	0.134	0.26	0.3	0.2	0.172	0.046	0.024	0.064	0.026
Zn	0	0	0	0	19.08	40.54	51.58	47.88	16.12	18.68	14.74	16.46	1.78	0.22	3	0.48
Ga	1.12	0.7	0.3	0.146	0.24	0.52	0.34	0.38	0.7	0.76	0.52	0.42	0.164	0.046	0.32	0.12
Rb	0.022	0.026	0.0146	0.0084	0.026	0.048	0.048	0.052	0.076	0.094	0.064	0.058	0.0166	0.08	0.172	0.0132
Sr	2.44	22.7	2.24	1.02	1.62	2.76	1.86	3.06	6.98	8.6	4.98	4.28	0.32	0.72	0.162	0.24
Y	0.098	0.54	1.52	1.22	1.18	2.18	0.78	1.66	0.28	0.34	0.138	0.068	3.12	6.54	1.88	2.4
Zr	63.96	41.72	11.44	4.42	266.98	174.14	286.3	224.84	361.42	587.2	507.78	114.32	7.4	1.7	24.64	3.2
Nb	0.0116	28.1	3.36	5.78	15.64	55.3	49.92	36.2	159.64	159.38	68.24	20.24	0.22	0.068	0.24	0.176
Mo	0	0	0	0	0	0	0	0	0	0	0	0	0.0148	0.006	0.038	0.0152
Sn	0.28	4.2	3.32	0.5	1.94	7.12	1.88	1.68	11.44	10.82	11.42	25.42	1.72	0.28	3.46	1.32
Sb	0	0	0	0	0	0	0	0	0	0	0	0	0.0074	0.0048	0.024	0.0076
Cs	0.0106	0.0082	0.0046	0.0028	0.0146	0.028	0.022	0.026	0.042	0.05	0.036	0.028	0.0032	0.0186	0.048	0.0032
Ba	0.022	0.05	0.22	0.0086	0.104	0.2	0.02	0.04	0.066	0.086	0.072	0.04	0.072	0.062	0.3	0.09
La	0.136	0.78	1.1	0.38	1.28	1.92	0.122	0.28	0.3	0.36	0.48	0.118	0.126	0.066	0.09	0.072
Ce	0.36	1.34	1.36	0.66	3.72	5.4	0.4	0.82	0.66	0.74	1.18	0.34	0.28	0.15	0.22	0.182
Pr	0.056	0.18	0.142	0.074	0.54	0.74	0.084	0.156	0.13	0.142	0.22	0.082	0.068	0.032	0.06	0.034
Nd	0.26	0.6	0.52	0.26	2.66	3.48	0.48	0.84	0.54	0.58	0.88	0.4	0.5	0.24	0.46	0.24
Sm	0.07	0.098	0.098	0.052	0.6	0.64	0.15	0.28	0.192	0.22	0.186	0.134	0.26	0.134	0.26	0.124
Eu	0.0072	0.006	0.0068	0.0032	0.038	0.036	0.0142	0.022	0.028	0.034	0.02	0.02	0.02	0.0136	0.032	0.0114
Gd	0.046	0.066	0.094	0.04	0.34	0.38	0.106	0.182	0.164	0.2	0.136	0.11	0.48	0.46	0.36	0.26
Tb	0.008	0.012	0.0164	0.0074	0.038	0.05	0.0178	0.032	0.03	0.038	0.022	0.0176	0.062	0.08	0.07	0.04
Dy	0.034	0.082	0.18	0.102	0.24	0.36	0.12	0.22	0.082	0.106	0.07	0.038	0.48	0.7	0.5	0.28
Ho	0.01	0.03	0.08	0.056	0.064	0.11	0.04	0.062	0.036	0.04	0.0194	0.0122	0.088	0.132	0.09	0.048
Er	0.052	0.2	0.48	0.4	0.32	0.58	0.24	0.34	0.22	0.24	0.084	0.082	0.26	0.34	0.32	0.134
Tm	0.0196	0.074	0.132	0.11	0.108	0.178	0.096	0.116	0.062	0.108	0.028	0.034	0.048	0.038	0.084	0.022
Yb	0.28	0.94	1.24	1	1.36	1.9	1.32	1.46	0.64	1.14	0.26	0.62	0.52	0.28	1.2	0.198
Lu	0.066	0.22	0.2	0.172	0.34	0.42	0.36	0.42	0.15	0.38	0.08	0.26	0.088	0.032	0.26	0.042
Hf	1.14	0.76	0.32	0.102	3.42	2.54	4.14	3.7	13.26	23.54	20.16	4.28	0.46	0.26	1.82	0.44
Ta	24.68	1.82	0.122	0.05	8.32	3.18	4.38	4.02	3.16	3.06	6.12	1.52	0.0094	0.0066	0.024	0.009
Pb	0.026	0.06	0.042	0.004	0.054	0.3	0.028	0.174	0.046	0.166	0.096	0.032	0.048	0.024	0.074	0.028
Th	0.011	0.126	0.096	0.0028	0.022	0.038	0.007	0.04	0.0058	0.0166	0.02	0.0044	0.094	0.03	0.052	0.036
U	0.007	0.0066	0.052	0.003	0.0164	0.064	0.0086	0.084	0.0064	0.034	0.034	0.0024	0.0182	0.0052	0.0124	0.0062

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR27	MR47B	MR47B	MR47B	MR47B	MR47B	MR47B	MR47B	MR47B	MR01D	MR01D	MR39	MR39	MR39
Local_spot	PyC3P1n	cpx1-1agr	cpx1-2agr	cpx7-1agr	cpx7-2agr	cpx5-1c	cpx5-1r	cpx5-3c	cpx5-4r	PyC1P1b	PyC1P2n	PyC6P1b-2	PyC6P2b	PyC6P3n
Facies	catác	catác	catác	catác	catác	catác	catác	catác	catác	microgran	microgran	maciça: eg-aug	maciça: eg-aug	maciça: eg-aug
Li	28.75	2.47	2.83	2.85	1.15	4.15	3.4	1.872	4.54	3.34	1.05	221.48	220.28	162.58
Be	5.9									1.61	0.55	19.32	28.15	11.31
P	31									19.72	8.66	80.75	82.89	72.81
Ca	0.46	500.29	500.29	500.29	500.29	500.29	500.29	500.29	500.29	0.38	0.37	4.8	4.8	3.79
Sc	4.72	3.39	3.03	3.47	0.956	2.416	2.434	2.095	3.18	4.01	2.062	1.9	1.64	1.93
Ti	8384.48	2181.9	1469.1	2637.13	1107.8	2941.44	2697.66	1333.66	2016.48	3737.74	2216.59	175.62	162.01	218.49
V	2.97	0.584	0.477	0.64	0.2029	0.292	0.45	0.346	0.692	0.274	0.177	3.06	2.8	2.13
Cr	5.75	<0.40	0.42	<0.45	<0.18	<0.37	<0.39	<0.27	<1.05	2.48	1.08	12.69	15.13	10.43
Mn	1444.97	251.17	192.98	259.18	109.69	200.6	225.53	170.92	273.65	974.54	362.19	54.25	81.19	43.76
Co	0.226	0.0401	0.0121	0.0376	0.0095	0.0376	0.033	0.0244	0.054	0.177	0.0336	0.092	0.201	0.098
Ni	<0.068	<0.56	<0.51	<0.64	<0.25	<0.52	<0.53	<0.36	<1.38	<0.072	<0.025	0.89	1.67	1.06
Cu	0.112	0.0418	0.0905	0.0615	0.0881	0.0718	0.0734	0.0416	0.063	0.161	0.117	4.61	8.6	3.73
Zn	323.8	42.02	39.74	48.08	7.55	51.58	64.3	40.36	53.16	263.08	97.48	11.6	15.15	8.23
Ga	7.93	1.052	1.034	1.135	0.481	1.391	1.532	0.703	1.435	4.79	1.82	69.01	38.66	44.43
Rb	0.03	0.0051	0.0172	0.0155	0.0151	0.0205	0.0285	0.0229	0.0234	0.285	0.267	346.72	495.51	282.45
Sr	1.178	0.56	0.5	0.62	1.3	0.5	0.53	0.37	1.41	0.575	0.523	22.07	18.56	16.33
Y	25.13	3.37	9.01	4.39	34.82	7.65	7.82	12.6	12.59	24.98	28.66	3.13	2.53	5.27
Zr	3297.32	903.65	789.19	960.72	197	861	705.2	657.29	877.94	3786.98	2058.66	104.19	100.79	81.98
Nb	0.49	0.208	1.112	0.562	0.403	5.27	1.187	3.2	5.5	1.272	0.435	2.53	2.13	2.44
Mo	0.469									0.251	0.259	0.34	0.42	0.76
Sn	117.81	38.46	24.6	37.99	6.55	27.4	25.67	19.83	33.44	28.05	14.52	4.43	5.21	4.08
Sb	<0.061									<0.038	0.0143	1.49	1.27	0.86
Cs	0.0075	<0.00175	0.00484	<0.00216	0.00239	<0.00180	0.00286	0.00268	<0.0051	0.0092	0.0084	37.58	33.74	26.21
Ba	<0.087	0.0513	0.0793	0.577	0.542	2.068	2.467	0.1691	0.372	<0.042	0.087	129.47	317.03	76.36
La	2.06	0.254	0.714	0.33	0.429	0.542	0.365	0.363	0.645	1.768	2.16	2.86	2.76	5.2
Ce	12.38	1.494	2.671	1.886	0.988	2.064	1.906	1.93	2.83	10.72	9.66	6.31	5.48	10.32
Pr	3.44	0.428	0.652	0.503	0.2055	0.416	0.436	0.499	0.592	2.76	2.04	0.693	0.551	1.292
Nd	22.68	2.89	4.18	3.32	1.24	2.283	2.626	3.34	3.75	18.06	10.75	2.48	1.98	5.03
Sm	16.28	1.507	2.237	1.625	0.874	0.85	1.373	1.925	1.917	8.92	4.04	0.65	0.61	0.98
Eu	0.742	0.0537	0.0827	0.0625	0.0641	0.0439	0.0566	0.0762	0.0738	0.347	0.154	0.054	0.082	0.132
Gd	14.71	1.376	2.649	1.6	2.07	1.091	1.656	2.91	3.19	8.29	3.98	0.35	0.57	0.73
Tb	3.07	0.2303	0.512	0.3	0.463	0.2076	0.352	0.664	0.764	1.615	0.766	0.09	0.038	0.111
Dy	18.22	1.341	3.58	1.845	4.98	1.647	2.607	5	6.24	9.62	6.14	0.48	0.194	0.68
Ho	3.17	0.2315	0.722	0.328	0.778	0.407	0.634	1.011	1.302	1.98	1.414	0.069	0.075	0.174
Er	10.37	0.953	2.83	1.383	2.391	2.183	3.61	4.15	3.46	7.6	6.42	0.52	0.241	0.378
Tm	3.18	0.298	0.788	0.47	0.404	0.797	1.134	1.234	0.85	2.42	1.739	0.06	0.03	0.052
Yb	42.53	4.19	9.27	6.73	3.89	11.13	16.03	16.2	10.53	30.76	20.38	0.25	0.23	0.27
Lu	11.17	0.971	1.929	1.676	1.15	2.89	3.74	3.54	2.37	6.67	4.11	0.071	0.037	0.076
Hf	204.87	70.1	50.71	60.42	10.18	23.71	21.11	22.71	51.13	112.45	42.87	2.61	2.33	1.74
Ta	0.0214	0.009	0.0122	0.0077	0.0142	0.497	0.1234	0.0183	0.0674	0.143	0.0358	3.81	3.8	2.83
Pb	0.316	0.0325	0.392	0.248	0.616	0.53	0.595	0.507	1.386	0.432	0.814	15.31	13.82	14.78
Th	<0.0121	0.0238	0.308	0.1448	0.343	1.3	0.287	1.314	2.75	0.0416	0.0321	1.11	0.854	1.71
U	0.0042	0.00086	0.0189	0.01089	0.0394	0.096	0.01227	0.353	0.415	0.0121	0.0032	0.612	0.613	0.561

Erro 2 sigma (2σ)

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR27	MR47B	MR47B	MR47B	MR47B	MR47B	MR47B	MR47B	MR47B	MR01D	MR01D	MR39	MR39	MR39
Local_spot	PyC3P1n	cpx1-1agr	cpx1-2agr	cpx7-1agr	cpx7-2agr	cpx5-1c	cpx5-1r	cpx5-3c	cpx5-4r	PyC1P1b	PyC1P2n	PyC6P1b-2	PyC6P2b	PyC6P3n
Facies	catac	catac	catac	catac	catac	catac	catac	catac	catac	microgran	microgran	maciça: eg-aug	maciça: eg-aug	maciça: eg-aug
Li	3.94	0.24	0.26	0.28	0.134	0.4	0.32	0.184	0.54	0.84	0.28	29.94	30.24	22.74
Be	3.46	0	0	0	0	0	0	0	0	1.08	0.38	12.3	17.2	7.56
P	6.02	0	0	0	0	0	0	0	0	3.46	1.5	16.46	17	14.84
Ca	0.038	38.72	37.86	39.64	40.96	40.32	38.86	36.7	51.16	0.03	0.026	0.32	0.32	0.26
Sc	0.5	0.26	0.22	0.26	0.08	0.188	0.184	0.152	0.3	0.38	0.178	0.5	0.48	0.46
Ti	708.6	158.52	105.48	194.34	83.36	219.16	196.84	94.34	175.32	856.44	520.98	23.4	22.34	28.54
V	0.32	0.044	0.036	0.05	0.0198	0.026	0.036	0.026	0.066	0.066	0.032	0.46	0.44	0.34
Cr	1.6	0.34	0.3	0.38	0.22	0.34	0.34	0.24	0.9	0.88	0.38	3.72	3.88	3.08
Mn	118.94	17.62	13.36	18.46	7.98	14.46	15.88	11.64	23.18	73.66	26.02	4.48	6.64	3.7
Co	0.07	0.011	0.0094	0.012	0.007	0.0112	0.0104	0.0072	0.026	0.044	0.0134	0.082	0.124	0.082
Ni	0.092	0.48	0.46	0.56	0.32	0.5	0.48	0.32	1.24	0.06	0.024	0.56	0.72	0.52
Cu	0.106	0.0126	0.0154	0.0166	0.0176	0.0186	0.0164	0.0114	0.038	0.084	0.048	1.12	1.62	0.9
Zn	29.82	2.9	2.7	3.36	0.56	3.66	4.44	2.7	4.48	24.92	9.06	2.12	2.54	1.64
Ga	0.74	0.076	0.074	0.084	0.04	0.104	0.11	0.05	0.13	0.44	0.164	6.4	3.82	4.32
Rb	0.022	0.0046	0.005	0.0058	0.0044	0.0058	0.006	0.0044	0.0144	0.046	0.032	30.26	43.86	25.5
Sr	0.14	0.48	0.42	0.52	0.34	0.46	0.46	0.32	1.2	0.072	0.054	2.02	1.76	1.56
Y	2.02	0.24	0.62	0.32	2.54	0.56	0.56	0.86	1.08	2.06	2.26	0.42	0.36	0.6
Zr	276.84	63.58	54.78	68.56	14.4	62.1	49.72	44.78	74.44	314.42	164.74	9.68	9.54	7.88
Nb	0.088	0.018	0.08	0.044	0.034	0.38	0.088	0.22	0.48	0.142	0.05	0.42	0.38	0.4
Mo	0.198	0	0	0	0	0	0	0	0	0.116	0.074	0.38	0.36	0.4
Sn	11.46	2.64	1.66	2.64	0.48	1.92	1.76	1.32	2.8	2.94	1.5	0.98	1.06	0.84
Sb	0.054	0	0	0	0	0	0	0	0	0.028	0.0136	0.4	0.36	0.26
Cs	0.0092	0.00138	0.00172	0.00186	0.00134	0.00174	0.00176	0.00132	0.0044	0.0056	0.0042	3.04	2.78	2.18
Ba	0.062	0.0072	0.0084	0.044	0.042	0.148	0.172	0.0134	0.038	0.044	0.038	14.44	34.8	9.08
La	0.22	0.02	0.052	0.026	0.036	0.042	0.028	0.026	0.06	0.198	0.22	0.38	0.38	0.6
Ce	1.02	0.106	0.184	0.134	0.074	0.15	0.134	0.13	0.24	0.9	0.78	0.66	0.6	1
Pr	0.32	0.032	0.046	0.038	0.0176	0.032	0.032	0.034	0.054	0.26	0.188	0.136	0.122	0.184
Nd	2.3	0.22	0.3	0.24	0.106	0.178	0.194	0.24	0.34	1.72	0.96	0.78	0.7	1.08
Sm	1.58	0.118	0.166	0.13	0.082	0.078	0.11	0.14	0.192	1.02	0.46	0.34	0.34	0.4
Eu	0.124	0.0068	0.0086	0.0078	0.0086	0.0064	0.0068	0.0074	0.012	0.068	0.03	0.054	0.078	0.084
Gd	1.8	0.106	0.19	0.124	0.164	0.09	0.126	0.2	0.3	1.18	0.56	0.28	0.4	0.38
Tb	0.28	0.0184	0.038	0.024	0.036	0.0178	0.026	0.046	0.07	0.158	0.072	0.054	0.034	0.058
Dy	1.82	0.104	0.26	0.142	0.38	0.13	0.192	0.34	0.54	1.1	0.68	0.26	0.16	0.28
Ho	0.32	0.0188	0.052	0.026	0.06	0.032	0.046	0.07	0.116	0.2	0.134	0.046	0.052	0.068
Er	1.06	0.074	0.2	0.106	0.184	0.166	0.26	0.28	0.3	0.66	0.5	0.22	0.17	0.172
Tm	0.3	0.024	0.056	0.036	0.032	0.06	0.082	0.084	0.078	0.24	0.156	0.042	0.038	0.038
Yb	4.4	0.3	0.64	0.48	0.3	0.8	1.12	1.1	0.9	3.04	1.94	0.24	0.24	0.2
Lu	0.98	0.07	0.134	0.12	0.086	0.2	0.26	0.24	0.2	0.6	0.36	0.05	0.046	0.044
Hf	19.78	4.86	3.46	4.24	0.74	1.68	1.46	1.52	4.28	11.1	4.18	0.74	0.7	0.54
Ta	0.017	0.0026	0.0028	0.0026	0.0036	0.04	0.012	0.003	0.0116	0.032	0.0104	0.48	0.5	0.38
Pb	0.074	0.0082	0.034	0.026	0.054	0.046	0.048	0.04	0.132	0.072	0.09	1.48	1.38	1.42
Th	0.0138	0.0038	0.024	0.0136	0.03	0.098	0.024	0.092	0.24	0.0172	0.0096	0.22	0.188	0.26
U	0.006	0.00056	0.0024	0.00194	0.0048	0.0086	0.00192	0.024	0.038	0.0078	0.0026	0.138	0.14	0.12

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR03-1-6	MR03-1-7	MR21-1-3	MR21-1-4	MR03-12-xt1-m	MR03-12-xt2-m	MR03-12-xt3-m
Local_spot	mantle	mantle	mantle	mantle	mantle	mantle	mantle
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil
Li	6.17	40.45	284	1.21	21.7	70.45	103.4
Be							
P							
Ca	1715.28	1715.28	2930.27	2930.27	1715.28	1715.28	1715.28
Sc	3.76	2.97	7.25	7.26	15.21	2.76	2.56
Ti	6758.04	6600.3	11091.6	15832.92	6511.36	6150.61	5831.44
V	0.888	0.1058	1.237	1.52	<0.132	<0.203	<0.212
Cr	3.38	3.14	4.1	4.22	<14.02	<20.83	<22.39
Mn					3772.11	2665.66	2964.21
Co	0.095	0.211	0.455	0.142	0.69	<0.57	0.73
Ni	<1.39	<1.63	<1.97	<2.73	22.08	42.32	30.47
Cu	0.197	0.198	9.5	0.799	<0.78	<1.10	<1.23
Zn					1165.49	1002.33	961.14
Ga	7.45	7.91	4.37	14.67	3.39	5.55	4.27
Rb	0.01205	0.413	6.23	83.91	0.165	0.245	0.26
Sr	8.075	3.03	3.78	1.785	8.05	11.96	12.75
Y	10.36	116.13	51.7	14.45	97.46	127.6	243.93
Zr	571.17	451.41	1070.49	1859.16	6446.74	817.21	651.81
Nb	6.44	60.82	47.91	30.17	270.7	264.3	344.86
Mo							
Sn	518.08	263.36	158.92	314.87	110.3	51.34	23.76
Sb							
Cs	<0.0066	0.0624	0.0648	0.353	<0.179	<0.27	<0.25
Ba	0.1295	0.268	1.029	2.465	0.666	3.54	2.09
La	1.301	8.63	15.3	8.25	8.51	17.37	27.03
Ce	5.24	25.67	38.81	23.32	28.78	45.32	63.73
Pr	1.137	5.02	6.49	3.67	5.4	8.21	9.88
Nd	6.33	27.18	30.97	17.39	24.3	35.67	45.37
Sm	1.8	9.5	8.32	4.51	6.63	11.49	15.96
Eu	0.0606	0.295	0.252	0.151	0.159	0.498	0.49
Gd	1.415	9.04	7.69	3.59	4.65	12.22	15.44
Tb	0.1872	1.49	1.239	0.57	0.984	2.31	2.74
Dy	1.35	14.05	9.69	3.54	8.88	17.04	24.18
Ho	0.35	4.95	2.686	0.8	3.03	3.79	6.43
Er	1.952	25.79	15.87	4.28	16.45	15	26.07
Tm	0.7	6.03	4.95	1.487	4.35	3.51	5.16
Yb	10.53	52.81	58.76	22.34	50.97	38.67	48.71
Lu	3.22	9.34	12.87	5.57	10.17	8.21	8.82
Hf	13.69	13.08	68.07	55.7	116.34	15.58	14.99
Ta	1.536	1.692	0.835	1.253	5.63	9.44	26.72
Pb	0.447	1.197	58.05	2.458	4.55	24.54	62.32
Th	0.0378	4.63	2.457	0.6	0.976	6.55	13.05
U	0.078	2.574	0.982	0.244	2.87	13.76	21.34

Tabela 9: Análises químicas de elementos-traços por LA-ICP-MS de clinopiroxênios do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR03-1-6	MR03-1-7	MR21-1-3	MR21-1-4	MR03-12-xt1-m	MR03-12-xt2-m	MR03-12-xt3-m
Local_spot	mantle	mantle	mantle	mantle	mantle	mantle	mantle
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil
Li	0.58	3.32	23.46	0.68	10.42	32.16	46.78
Be	0	0	0	0	0	0	0
P	0	0	0	0	0	0	0
Ca	126.26	130.66	208.22	220.06	288.06	385.86	391.6
Sc	0.28	0.24	0.52	0.56	2.16	0.76	0.76
Ti	475.22	471.4	757.82	1115.02	1240.7	1340.9	1281.52
V	0.07	0.02	0.092	0.12	0.12	0.176	0.194
Cr	1.92	1.98	1.72	2.52	11.94	18	19.32
Mn	0	0	0	0	494.78	449.28	506.24
Co	0.034	0.042	0.054	0.054	0.34	0.48	0.52
Ni	1.22	1.44	1.74	2.34	18.66	35.86	26.06
Cu	0.074	0.086	0.68	0.148	0.66	0.96	1.04
Zn	0	0	0	0	150.62	167.56	162.88
Ga	0.5	0.56	0.3	1	0.62	1.14	1
Rb	0.0198	0.042	0.42	5.64	0.28	0.4	0.44
Sr	13.68	5.1	2.04	3.02	13.78	20.36	21.74
Y	0.74	8.22	3.5	1.02	13.72	22.48	43.46
Zr	39.8	32.06	72.5	129.92	847.24	138.32	111.9
Nb	0.46	4.3	3.24	2.12	34.76	44	58.16
Mo	0	0	0	0	0	0	0
Sn	34.3	17.8	10.28	21.06	24.24	12.88	6.62
Sb	0	0	0	0	0	0	0
Cs	0.0056	0.0106	0.0102	0.032	0.152	0.22	0.22
Ba	0.0158	0.026	0.076	0.178	0.182	0.66	0.46
La	0.094	0.6	1	0.58	1.14	2.96	4.64
Ce	0.36	1.74	2.52	1.58	3.7	7.54	10.72
Pr	0.08	0.34	0.42	0.26	0.72	1.4	1.7
Nd	0.46	1.88	2.06	1.22	3.38	6.24	7.98
Sm	0.154	0.7	0.6	0.38	1.16	2.28	3.1
Eu	0.0096	0.03	0.026	0.022	0.082	0.162	0.162
Gd	0.122	0.66	0.54	0.3	0.9	2.48	3.12
Tb	0.0182	0.11	0.09	0.05	0.17	0.44	0.52
Dy	0.116	1	0.68	0.3	1.6	3.5	4.96
Ho	0.03	0.34	0.186	0.068	0.48	0.74	1.22
Er	0.152	1.8	1.06	0.32	2.26	2.66	4.58
Tm	0.054	0.42	0.34	0.114	0.6	0.64	0.92
Yb	0.74	3.66	3.88	1.58	6.88	6.74	8.56
Lu	0.22	0.64	0.86	0.4	1.36	1.42	1.56
Hf	0.94	0.92	4.48	3.8	14.94	2.74	2.68
Ta	0.116	0.132	0.068	0.104	0.82	1.68	4.68
Pb	0.034	0.088	3.76	0.176	0.76	4.32	10.84
Th	0.007	0.32	0.172	0.054	0.188	1.24	2.44
U	0.0082	0.178	0.068	0.022	0.48	2.66	4.14

Tabela 10: Análises químicas de elementos-traços por LA-ICP-MS em cristais de britholita do Plúton Papanduva, Complexo Morro Redondo

Amostra	mr03-1-1	mr03-1-2	mr03-2-1	mr03-2-2	mr03-1-3	mr03-1-xt2-1	mr03-1-xt3-1	mr03-2-3	mr03-2-4	mr03-2-5	mr03-1-1t	mr03-1-2t
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil
Li	125.4	117.27	160.9	82.57	<4.74	<5.20	<4.82	<4.92	<4.63	<3.37	<25.87	<5.72
Be	<1.43	<1.43	<1.53	<1.68	1.44	<1.22	<1.19	<1.20	<1.13	1.05	<5.71	<1.28
Mg	27.74	18.91	36.43	22.42	46.06	49.24	58.56	76.91	64.66	55.21	45.36	27.33
Ca	28373.63	28373.63	23799.55	23799.55	28373.62	28373.62	28373.62	23799.54	23799.54	23799.54	28373.63	28373.63
Sc	<0.34	<0.32	<0.35	<0.38	<0.25	<0.28	0.32	<0.25	<0.24	<0.173	<1.35	<0.36
Ti		10.87	6.66	2.83	2.45		3.1				<10.24	<1.81
V	<0.193	<0.182	<0.195	<0.214	<0.117	<0.123	<0.118	<0.117	<0.108	<0.080	<0.74	<0.174
Cr	<5.29	<5.55	<5.60	<6.23	<6.66	<7.39	<6.88	<6.86	<6.43	<4.58	2.13	
Mn	354.46	412.97	399.28	433.21	286.26	293.56	274.6	321.54	315.15	264.74		
Co	<0.42	<0.43	<0.45	<0.49	<0.26	<0.27	<0.25	<0.26	<0.24	<0.175	<2.29	<0.57
Ni	8.5	7.23	10.29	7.08	7.95	5.93	5.37	9.05	4.99	6.18	4.9	2.93
Cu	<0.99	<1.05	<1.08	<1.12	<0.54	<0.60	<0.58	<0.55	<0.54	<0.38	<3.43	<0.70
Ga	81.45	81.75	85.08	95.03	85.63	92.94	77.77	93.79	98.29	60.99	22.65	32.39
Rb	<0.27	0.98	0.51	1.09	0.758	0.819	0.936	0.6	0.613	0.43	<1.22	1.2
Sr	1208.43	1627.6	1221.46	1138.52	3379.4	3259.8	3855.92	3192.4	3202	4497.25		
Y	1501.96	<0.114	<0.108	<0.126	199.62	498.6	543.61	<0.086	<0.089	<0.065	8709.98	<0.065
Zr	<0.39	<0.40	0.78	0.48	<0.29	<0.27	<0.24	<0.26	<0.26	3.32	<1.71	1.03
Nb	7.95	15.25	16.16	17.63	10.93	10.58	9.29	11.89	10.95	7.77	2.95	11
Sn	<1.33	<1.38	<1.42	<1.54	<1.13	<1.25	<1.16	<1.16	<1.08	<0.77	0.48	0.143
Cs	<0.134	<0.129	<0.144	<0.149	<0.057	<0.068	<0.062	<0.063	<0.056	<0.043	<0.34	<0.085
Ba	602.41	615.27	640.27	691.67	471.16	434.8	362.25	473.21	454.47	343.84	820.3	308.46
Sm	9476.93	11441.44	11853.11	12181.27	7741.35	7271.81	5947.86	8676.43	8146.57	5717.28	15444.45	5340.09
Eu	260.03	329.54	321.81	329.4	222.38	233.45	198.02	268.59	214.15	154.86	402.11	126.36
Gd	5325.82	7707.69	8764.73	8592.92	4281.12	4895.69	3982.3	5794.38	5573.79	4138.49	9260.26	1837.43
Tb	546.44	801.27	785.72	768	491.3	550.06	447.37	608.76	533.01	379.94	1014.82	232.05
Dy	2372.14	3736.41	3271.52	3250.16	2408.95	2244.09	2065.87	2204.3	2121.53	1593.8	4619.98	780.79
Ho	285.81	469.37	408.43	392.55	379.42	381.69	295.82	331.08	298.12	221.33	679.15	96.87
Er	522.07	871.37	723.6	716.92	709.67	708.23	504.5	571.28	525.58	386.51	1313.8	164.92
Tm	40.78	72.64	57.74	58.48	56.47	62.51	44.17	50.54	45.22	33.76	121.05	13.39
Yb	168.42	293.02	248.57	244.3	237.98	278.41	233.47	219.45	189.45	160.8	509.16	46.48
Lu	12.23	22.23	19.66	19.14	16.49	17.73	16.79	15.8	14.19	13.47	35.36	3.69
Hf	0.136	0.143	0.111	0.179	0.272	0.171	0.197	0.226	0.127	0.444	0.488	0.0377
Ta	0.08	<0.082	<0.089	<0.102	0.096	<0.059	<0.043	0.052	<0.045	0.226	0.049	<0.0135
Pb	1713.76	1857.57	1849.43	2032.37	1184.49	1226.09	947.59	1408.85	1460.59	1231.61	2468.58	217.53
Th	1019.52	1530.75	1170.29	1296.89	964.91	1024.52	732.73	873.1	946.85	405.47	2394.87	251.19
U	67.48	81.64	59.18	61.46	66.29	64.58	52.62	45.94	44.35	36.88	124.35	7.91

protomil = protomilonítica

Tabela 10: Análises químicas de elementos-traços por LA-ICP-MS em cristais de britholita do Plúton Papanduva, Complexo Morro Redondo

Amostra	mr03-1-1	mr03-1-2	mr03-2-1	mr03-2-2	mr03-1-3	mr03-1-xt2-1	mr03-1-xt3-1	mr03-2-3	mr03-2-4	mr03-2-5	mr03-1-1t	mr03-1-2t
Facies	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil	protomil
Erro 2 sigma (2σ)												
Li	1687.86	1578.4	2165.44	1111.72	10.7	9.56	7.58	7.66	8.92	7.82	88.4	47.8
Be	1.22	1.22	1.34	1.46	1.12	1.1	1.02	1.02	1.02	0.8	5.28	1.2
Mg	50.18	34.86	65.5	41.2	155.26	166.08	196.34	256.92	216.3	184.32	42.66	23.58
Ca	1904.06	1904.72	1623.4	1634.34	1865.22	1872.24	1866.34	1578.96	1575.22	1554.52	3104.46	2737.72
Sc	0.28	0.28	0.3	0.32	0.22	0.24	0.22	0.22	0.2	0.146	1.16	0.3
Ti	15.94	36.5	23.12	12.14	8.32	19.68	9.2	7.48	7.54	5.14	9.24	3.2
V	0.16	0.154	0.162	0.176	0.098	0.104	0.098	0.1	0.092	0.066	0.64	0.144
Cr	4.52	4.72	4.8	5.38	6.26	7.1	5.84	8.5	9.16	4.22	1.6	0.74
Mn	37.34	43.48	42.18	45.84	57.54	59.02	55.2	64.66	63.36	53.2	549.14	458.36
Co	0.36	0.36	0.38	0.42	0.22	0.22	0.22	0.22	0.2	0.148	1.98	0.52
Ni	8.48	7.22	10.26	7.08	7.54	5.68	5.14	8.58	4.78	5.86	0.78	0.32
Cu	0.86	0.88	0.92	0.96	0.46	0.52	0.48	0.5	0.46	0.32	2.96	0.6
Ga	9.94	9.98	10.42	11.64	5.58	6.06	5.08	6.14	6.42	3.96	4.12	5.28
Rb	0.24	0.24	0.26	0.28	0.152	0.164	0.16	0.148	0.144	0.104	1.06	0.34
Sr	683.04	919.94	690.5	643.66	7859.38	7581.26	8967.62	7424.52	7446.82	10459.06	3.48	1.82
Y	110.26	0.082	0.076	0.09	40.88	102.12	111.3	0.098	0.108	0.08	968.98	0.048
Zr	0.34	0.36	0.4	0.42	0.24	0.24	0.22	0.24	0.22	0.42	1.42	0.46
Nb	1.1	2.08	2.2	2.4	1.02	0.98	0.88	1.1	1.02	0.72	0.52	1.22
Sn	1.14	1.18	1.22	1.32	0.98	1.08	1.08	0.98	0.92	0.66	0.34	0.088
Cs	0.112	0.108	0.12	0.126	0.048	0.058	0.052	0.052	0.048	0.036	0.28	0.07
Ba	57.46	58.68	61.32	66.36	80.1	73.94	61.6	80.5	77.3	58.42	87.04	30.72
Sm	1141.16	1377.76	1430.94	1472.16	489.28	460.56	376.1	551.1	516.78	360.1	2355.02	790.58
Eu	23.88	30.24	29.68	30.44	36.66	38.5	32.66	44.3	35.32	25.52	43.5	12.86
Gd	345.82	500.48	574.02	564.84	501.9	574.28	466.92	680.26	654.12	484.66	1048.72	197
Tb	36.4	53.36	52.76	51.74	33.4	37.46	30.42	41.56	36.34	25.76	97.12	20.52
Dy	247	389	341.78	340.06	193.64	180.64	166.12	177.76	170.94	127.84	515.86	82.4
Ho	28.48	46.76	40.84	39.32	39.86	40.14	31.08	34.84	31.36	23.22	63.86	8.4
Er	33.58	55.96	46.92	46.68	77.84	77.74	55.36	62.78	57.74	42.36	135.88	15.96
Tm	3.5	6.2	4.96	5.04	3.66	4.06	2.88	3.3	2.94	2.18	11.36	1.16
Yb	17.56	30.4	25.92	25.52	20.48	23.98	20.1	18.96	16.36	13.82	55.38	4.78
Lu	1.02	1.8	1.6	1.58	1.1	1.2	1.12	1.06	0.96	0.9	3.34	0.32
Hf	0.072	0.076	0.084	0.098	0.068	0.064	0.058	0.072	0.06	0.076	0.106	0.0134
Ta	0.076	0.07	0.078	0.082	0.046	0.048	0.042	0.048	0.038	0.05	0.048	0.011
Pb	212.52	230.36	229.9	252.9	159.74	165.42	127.8	190.2	197.12	165.96	232.04	18.84
Th	67.32	101.04	77.92	86.66	74.96	79.7	56.94	68.06	73.74	31.44	226.06	21.88
U	7.76	9.38	6.84	7.1	13.2	12.86	10.48	9.16	8.84	7.34	11.48	0.68

Tabela 11: Análises químicas de elementos-traços por LA-ICP-MS de cristais de nacarenioobsita do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR-02A-nacar2-1	MR-02A-nacar2-2	MR-02A-nacar3-1	MR-02A-nacar3-2	MR-140-nacar5-1	MR-140-nacar5-2
Facies	protomil	protomil	protomil	protomil	protomil	protomil
Li	8.71	9.63	<1.51	8.57	7.35	8.16
Ca	130147.03	130147.04	130147.04	130147.04	130147.03	130147.03
Sc	1.113	1.342	3.92	1.11	0.615	1.704
Ti	4306.09	5411.06	4423.66	6405.37	3169.38	4128.31
V	<0.028	<0.027	<0.068	<0.025	0.036	<0.029
Cr	<2.44	<2.46	7.87	<2.32	<2.19	<2.49
Mn	8.38	31.3	5.84	7.93	9.71	17.33
Co	0.27	0.202	0.3	0.283	0.178	1.766
Ni	<3.41	<3.07	<7.55	<2.52	<15.30	<7.47
Cu	0.401	0.608	4.29	0.406	0.263	0.272
Zn	85.1	91.47	90.19	89.61	74.81	82.73
Ga	38.36	39.65	80.28	38.12	31.54	33.21
Rb	0.871	1.136	0.875	0.69	1.42	3.52
Sr	635.48	636.62	756.25	655.17	624.11	665.71
Y	<0.042	<0.099	2257.92	<0.057	<0.036	<0.040
Zr	17.92	48.75	255.7	28.68	10.19	52.36
Sn	3.35	2.94	6.4	2.93	2.03	3.13
Cs	1.208	1.156	1.115	1.119	1.147	3.21
Ba	248.93	253.01	190.91	249.73	195.71	209.08
La	<0.117	<0.22	<0.32	<0.107	<0.062	<0.068
Ce	<0.131	<0.31	<0.49	<0.19	<0.061	<0.063
Pr	661.53	1397.78	1939.96	929.68	836.29	839.08
Nd	52143.22	56570.27	50722.07	60121.83	43563.74	46415.68
Sm	8955.86	9524.57	11940.15	9828.44	9338.1	10132.54
Eu	257.18	276.74	276.74	283.63	270.72	274.04
Gd	5450.51	5348	6806.37	5710.95	5716.98	6039.28
Tb	616.52	681.01	616.97	681.39	697.05	696.99
Dy	2420.04	2694.78	1878.47	2703.21	2759.21	2610.06
Ho	296.1	341.75	177.46	334.2	361.02	331.66
Er	580.8	677.33	314.94	650.81	678.55	624.77
Tm	40.13	50.97	15.71	48.95	45.94	44.86
Yb	169.75	221.94	65.62	209.97	174.45	190.85
Lu	11.31	15.55	4.61	14.96	11.35	13.83
Hf	4.75	6.15	5.73	5.32	2.29	12.16
Ta	<0.0226	<0.081	4183.28	<0.0211	<0.0146	56.58
Pb	13.08	13.97	8.14	15.31	22.44	26.3
Th	33.4	46.76	4.26	41.64	7.68	17.92
U	26.36	25.37	11.52	23.84	26.66	21.54

Tabela 11: Análises químicas de elementos-traços por LA-ICP-MS de cristais de nacarenioobsita do Plúton Papanduva, Complexo Morro Redondo

Amostra	MR-02A-nacar2-1	MR-02A-nacar2-2	MR-02A-nacar3-1	MR-02A-nacar3-2	MR-140-nacar5-1	MR-140-nacar5-2
Facies	protomil	protomil	protomil	protomil	protomil	protomil
Erro 2 sigma (2σ)						
Li	0.88	0.94	1.94	0.86	0.78	0.86
Ca	8273.42	8273.34	8641.46	8272.6	8284.3	8284.68
Sc	0.168	0.174	0.7	0.16	0.134	0.192
Ti	279.34	351.64	300.16	418.1	207.44	270.7
V	0.022	0.024	0.098	0.02	0.028	0.028
Cr	2.08	2.08	8.2	1.98	1.98	2.22
Mn	0.58	2	0.94	0.56	0.68	1.14
Co	0.06	0.06	0.22	0.06	0.068	0.154
Ni	2.96	2.62	9.42	2.14	17.42	7.08
Cu	0.092	0.108	0.78	0.092	0.092	0.094
Zn	5.3	5.7	6.8	5.58	4.74	5.22
Ga	2.36	2.44	5.28	2.36	1.96	2.06
Rb	0.074	0.09	0.184	0.064	0.112	0.24
Sr	39.22	39.28	50.22	40.4	38.62	41.38
Y	0.028	0.084	145.46	0.04	0.024	0.026
Zr	1.4	3.32	18.84	2.06	0.94	3.6
Sn	0.38	0.38	1.42	0.38	0.36	0.4
Cs	0.086	0.082	0.15	0.08	0.084	0.22
Ba	15.18	15.42	12.1	15.22	11.94	12.76
La	0.126	0.38	0.34	0.112	0.048	0.056
Ce	0.154	0.7	0.66	0.26	0.05	0.052
Pr	40.36	85.26	121.38	56.74	51.02	51.18
Nd	3192.44	3466.56	3187.24	3691.42	2661.3	2835.18
Sm	548.16	582.98	749.56	601.6	571.94	620.52
Eu	15.68	16.88	17.52	17.28	16.54	16.74
Gd	334.3	328	428.22	350.2	351.2	370.76
Tb	37.86	41.82	38.96	41.82	42.88	42.88
Dy	149.22	166.12	119.3	166.6	170.2	160.88
Ho	18.3	21.12	11.42	20.64	22.36	20.52
Er	35.86	41.8	20.46	40.12	42	38.64
Tm	2.5	3.16	1.18	3.04	2.86	2.8
Yb	10.56	13.76	4.96	13.02	10.9	11.92
Lu	0.72	0.98	0.46	0.94	0.72	0.88
Hf	0.34	0.44	0.74	0.38	0.2	0.82
Ta	0.0142	0.062	269.22	0.0132	0.009	3.6
Pb	0.84	0.9	0.92	0.98	1.44	1.68
Th	2.1	2.94	0.46	2.62	0.52	1.16
U	1.6	1.54	0.82	1.46	1.64	1.32

protomil = protomilonítica

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	MR-161-B-I-12	MR-161-B-I-5	MR-161-B-II-9	MR-161-B-II-11	MR-161-B-II-5	MR-186A-CI-7	MR-186A-CI-13	MR-186A-CI-11	MR-186A-CII-6	MR-186A-CII-3	MR-186A-CII-16
Pluton	Quiriri										
Associação	Aluminosa										
Si	147617.34	147617.34	147617.34	147617.34	147617.33	147617.33	147617.34	147617.34	147617.34	147617.34	147617.34
P	692.36	492.35	774.44	1408.63	1225.59	683.75	678.85	556.19	39141.64	754.77	779.42
Sc	306.33	233.05	272.42	331.11	292.39	314.77	317.26	275.32	358.9	240.57	239.07
Ti	7.99	9.89	9.38	13.6	10.34	10.67	16.8	14.97	165.61	18.67	16.7
Mn	<0.70	<0.78	1.95	4.16	9.8	<0.87	3.94	<0.97	199.49	3.42	4.76
Sr	1.46	1.18	1.81	1.11	4.71	1.35	2.05	1.36	15.41	1.97	2.52
Y	3862.16	2821.15	4490.5	3554.21	5546.83	3861.64	2727.31	3164.88	6855.47	3909.55	3877.92
Zr	816599.81	592542.5	667557.5	825746.25	665583.25	700242.88	660465.25	936547.75	836282.56	621407.25	666365.69
Nb	62.56	36.97	51.23	47.19	68.24	50.12	45.9	63.81	114.73	72.41	71.47
Mo	33.49	30.75	37.34	34.98	37.49	40.56	36.04	39.03	44.49	32.97	37.24
Ba	1.37	<0.31	1.42	1.96	9.74	0.84	2.05	1.8	20.82	5.99	1.63
La	0.429	0.49	2.64	3.73	2.06	0.55	3.06	1.51	462.5	6.61	4.87
Ce	58.73	40.75	50.03	27.23	51.46	49.32	43.31	54.98	1252.36	52.34	58.19
Pr	0.355	0.203	1.2	0.91	1.56	0.6	1.41	0.78	219.01	2.46	1.45
Nd	5.41	4.02	9.16	5.87	14.68	7.29	10.49	6.48	1099.1	13.59	12.86
Sm	9.95	6.81	14.74	9.29	20.93	14.15	12.64	11.06	323.01	15.69	12.14
Eu	0.61	0.567	0.77	0.83	0.97	0.81	1.28	0.94	6.01	1.09	0.86
Gd	70.25	42.87	84.59	40.9	94.01	78.56	55.05	45.13	461.37	79.87	88.63
Tb	21.52	13.63	27.81	18.94	36.03	23.67	20.47	18.17	90.46	25.65	29.39
Dy	290.54	237.94	370.08	313.23	504.38	342.88	281.11	226.42	755.13	336.2	338.72
Ho	96.3	92.2	160.78	133.6	190.29	117.42	112.05	98.6	242.52	131.81	160.38
Er	505.67	396.67	685.07	431.11	878.71	589.23	477.48	481.92	904.1	543.66	615.38
Tm	119.73	90.23	138.22	98.9	166.43	133.64	97.45	118.47	173.37	123.56	101.05
Yb	903.22	811.22	1205.86	877.47	1577.1	987.06	892.91	892.47	1404.02	1086.85	988.59
Lu	185.31	148.76	218.11	136.7	263.97	189.47	137.3	182.31	236.23	198.56	230.32
Hf	17771.68	14505.96	15916.65	9021.27	16776.03	17131.89	12341.69	17000.22	17325.15	13530.16	16982.01
Ta	5.49	2.55	2.61	1.57	3.83	3.47	2.95	3.31	4.45	3.76	3.86
Pb206	190.18	86.74	817.61	177.49	175.8	157.33	128.15	109	245.59	124.04	156.43
Pb208	41.18	16.52	1505.3	124.44	60.79	32.63	74.21	30.58	189.76	28.88	41.54
Th	794.55	342.86	587.7	217.29	743.89	601.71	431.3	528.47	879.8	527.17	638.89
U	378.45	224.69	281.05	151.23	389.38	331.24	271.13	300.24	744.56	351.02	358.86

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	MR-161-B-I-12	MR-161-B-I-5	MR-161-B-II-9	MR-161-B-II-11	MR-161-B-II-5	MR-186A-CI-7	MR-186A-CI-13	MR-186A-CI-11	MR-186A-CII-6	MR-186A-CII-3	MR-186A-CII-16
Pluton	Quiriri										
	Erro 2 sigma (2σ)										
Si	9476.5	9437.82	9520.02	10175.04	9573.68	9483.3	9536.18	9572.9	9651.96	9505.9	9564.78
P	1269.7	933.8	1526.04	2898.44	2637.42	1806.18	1892.58	1637.54	121540.36	2474.64	2696.58
Sc	75.84	58.78	70.4	88.84	80	98.78	103.4	93.24	126.24	87.78	90.62
Ti	5.06	5.54	6.32	13.48	6.74	6.66	10.46	10.54	91.6	12.06	11.7
Mn	0.7	0.68	1.16	2.44	2.66	0.8	1.44	0.96	57.94	1.38	1.84
Sr	0.46	0.36	0.58	0.56	1.5	0.52	0.78	0.58	6	0.82	1.1
Y	1090.64	810.86	1320.32	1075.1	1725.52	1379.38	1010.88	1217.3	2736.02	1618.02	1663.96
Zr	321782.04	238377.82	275497.94	351224.96	292255.32	357179.34	350589.5	517438.28	480881	371732.26	414574.84
Nb	9.66	5.8	8.24	8.34	11.5	9.48	9.02	12.94	23.96	15.6	15.94
Mo	10.64	9.84	12.32	13.28	13.1	15.78	14.64	16.4	19.4	14.74	17.26
Ba	0.72	0.34	0.8	1.84	4	0.62	1.22	1.2	10.38	3.2	1.16
La	0.15	0.16	0.8	1.28	0.68	0.22	1.14	0.6	177.9	2.66	2.06
Ce	14.9	10.52	13.2	7.58	14.36	15.76	14.36	18.9	445.74	19.34	22.28
Pr	0.142	0.09	0.42	0.46	0.58	0.26	0.6	0.36	92.74	1.1	0.7
Nd	3.02	2.24	5.12	4.26	8.48	4.74	7	4.58	757.4	9.82	9.66
Sm	4.1	2.82	6.12	4.9	8.96	6.62	6.16	5.58	159.94	8.14	6.56
Eu	0.24	0.198	0.3	0.54	0.38	0.32	0.48	0.4	2.08	0.44	0.38
Gd	23.74	14.74	29.66	16.32	34.82	33.04	24.16	20.62	214.62	38.66	44.46
Tb	5.54	3.56	7.4	5.42	10.06	7.46	6.7	6.16	31.42	9.22	10.92
Dy	84.1	69.32	109.22	95.14	154.5	116.26	98.1	81.32	278.3	127.34	131.84
Ho	29.22	28.28	50.12	42.82	62.04	42.98	42.32	38.44	97.46	54.6	68.46
Er	172.6	136.62	239.42	154.36	320.04	239.44	199.92	207.88	401.58	248.54	289.52
Tm	42.08	32	49.74	36.54	62.42	55.92	42.04	52.64	79.32	58.18	48.98
Yb	311.1	281.9	425.26	317.08	579.64	404.78	377.3	388.52	629.42	501.44	469.44
Lu	42.78	34.64	51.56	33.34	65.02	51.94	38.8	53.04	70.76	61.16	73
Hf	5699.92	4689.16	5215.26	3014.62	5717.06	6488.52	4810.58	6819.62	7151.86	5743.56	7411.44
Ta	0.94	0.46	0.52	0.64	0.76	0.7	0.64	0.74	1.02	0.82	0.9
Pb206	40.22	18.62	176.58	40.9	40.04	39.84	33.6	29.54	68.22	35.48	46.12
Pb208	9	3.7	333.66	29.04	14.32	8.64	20.16	8.68	54.78	8.68	12.86
Th	192.44	83.84	145.88	55.56	192.46	173.56	128.18	161.78	277.38	171.04	213.32
U	98.32	59.14	75.38	41.84	109.56	105.22	89.02	101.86	260.9	127	134.04

Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa

Amostra	MR-186A-CII-11	MR-201A-AI-6	MR-201A-AII-11	MR-201A-AII-13	MR-201A-AII-2	GUA-16-4	GUA-16-6	GUA-16-7	GUA-16-13	GUA-16-11	GUA-16-12	GUA-16-3
Pluton	Quiriri					Guaraú						
Associação	Aluminosa											
Si	147617.34	147617.34	147617.34	147617.34	147617.34	147617.41	147617.41	147617.41	147617.41	147617.41	147617.41	147617.41
P	614.75	405.23	461.62	412.87	2326.41	149.01	546.49	289.05	207.18	199.53	162.41	214.67
Sc	292.94	213.79	274.63	272.91	277.92	235.64	238.29	246.43	232.74	297.12	198.38	189.52
Ti	13.65	5.8	7.33	16.42	25.78	7.83	15.43	15.7	25.65	23	16.43	7.03
Mn	2.1	1.45	0.84	10.5	48.59	5.7	15.17	12.76	4.97	34.66	21.8	284.31
Sr	2.01	1.12	1.6	2.47	7.08	2.72	1.18	1.09	2.41	5.1	3.41	7.13
Y	3881.2	3103.16	3192.62	3640.71	4069.84	2317.06	1489.56	1955.85	4410.94	3625.21	2302.3	5659.96
Zr	744339.38	512170.69	523019.56	577694.63	548057.69	455807.31	538512.44	519315.5	458164.28	668948.19	473946	534484.75
Nb	45.6	55.42	44.41	110.88	137.53	83.96	44.09	37.87	45.71	141.39	88.23	148.21
Mo	37.99	46.54	42.93	46.57	38.82	42.21	33.42	35.95	38.62	58.35	35.66	35.16
Ba	4.5	<0.208	<0.21	5.94	8.58	2.24	0.34	5.38	0.44	6.47	4.77	4.94
La	8.96	9.86	2.21	16.34	114.32	1.98	53.87	8.34	11.53	45.14	8.1	32.28
Ce	69.51	74.57	47.62	84.85	298.15	35.85	99.54	26.45	65.65	168.8	36.88	200.97
Pr	3.02	2.35	0.62	3.52	36.97	1.21	15.68	1.67	4.49	16.35	3.62	35.41
Nd	16.88	12.65	7.03	17.75	196.96	7.72	60.82	11.22	38.33	87.59	20.78	160.44
Sm	11.57	10.39	10.31	13.65	60.82	12.8	21.78	13.23	46.14	45.4	27.52	78.14
Eu	0.76	0.25	1.01	0.87	1.89	0.162	0.256	0.95	0.67	2.14	0.131	0.235
Gd	60.44	42.88	67.58	71.67	124.87	70.57	60.57	55.74	186.54	142.74	80.08	146.31
Tb	24.3	16.09	23.37	27.05	34.83	22.33	18.37	18.61	53.14	46.95	29.98	36.17
Dy	317	252.28	315.13	339.51	405.89	314.65	206.11	214.15	514.12	419.41	287.2	428.77
Ho	132.59	100.04	115.47	133.74	146.61	96.32	54.04	62.83	182.77	133.7	93.13	183.06
Er	549.74	457.19	497.7	562.31	621.23	486.88	262.87	298.21	792.64	626.17	391.55	878.44
Tm	122.29	94.2	98.03	122.72	117.9	92.03	47.49	50.2	146.43	125.67	91.1	186.78
Yb	988.64	862.65	842.8	1254.48	1030.95	783.29	422.68	420.3	1276.64	1053.9	752.09	1766.83
Lu	171.75	180.23	158.04	217.2	187.99	127.24	80.22	84.53	227.99	184.21	109.73	335.28
Hf	12312.19	16610.62	12871.5	16505.13	13098	13709.67	11964.53	9783.14	11056.22	18093.31	11868.9	22242.46
Ta	3.2	7.07	2.33	6.78	2.23	23.48	1.99	1.34	2.47	5.88	3.5	23.47
Pb206	239.96	154.31	93.51	163.54	80.07	145.3	40.79	26.42	70.03	781.92	175.17	512.75
Pb208	113.36	21.5	20.55	35.53	16.88	48.76	11.73	4.76	16.09	152.29	68.41	180.31
Th	619.56	591.5	451.85	908.31	555.01	453.13	135.36	100.18	342.43	883.87	632.8	1178.79
U	353	431.99	239.16	515.17	349.84	388.39	132.69	53.73	230.39	749.68	289.45	1452.44

Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa

Amostra	MR-186A-CII-11	MR-201A-AI-6	MR-201A-AII-11	MR-201A-AII-13	MR-201A-AII-2	GUA-16-4	GUA-16-6	GUA-16-7	GUA-16-13	GUA-16-11	GUA-16-12	GUA-16-3
Pluton	Quiriri					Guaraú						
Erro 2 sigma (2σ)												
Si	9610.04	9875.96	9519.64	9635.66	9636.42	9503.76	9506.68	9627.04	9663.24	10309.86	9528.56	9609.82
P	2244.24	842.92	941.08	829.32	4614.46	128.46	484.88	270.24	204.22	223.5	178.38	249.76
Sc	115.2	92.5	123.44	127.96	135.78	29.66	30.4	32.28	31.24	42.02	27.66	27.36
Ti	11.1	7.8	6.72	15.2	23.5	5.78	9.46	10.66	16.32	25.8	10.76	6.68
Mn	1.44	1.28	0.78	3.34	14.92	2.78	7.14	6.24	2.74	17.92	11.24	149.88
Sr	0.92	0.36	0.32	0.5	1.2	0.58	0.3	0.32	0.62	1.38	0.8	1.66
Y	1725.58	581.2	621.08	738.28	859.6	463.54	303.88	408.64	946.28	803.5	524.68	1334.48
Zr	481339.9	264089.94	280467.78	322283.66	317936.88	139389.96	168701.22	167333.62	152330.06	230440.68	169117.16	198288.86
Nb	10.58	29.02	24.2	63.06	81.58	18.9	10.14	8.98	11.1	35.24	22.44	38.88
Mo	18.24	29.02	27.46	31.16	27.08	12.92	10.5	11.76	12.98	20.88	12.38	12.76
Ba	2.74	0.134	0.22	2.2	3.12	0.84	0.28	1.92	0.44	3.1	1.7	1.88
La	3.88	3.04	0.72	5.4	39.26	0.46	11.24	1.84	2.58	10.26	1.9	7.64
Ce	27.58	24.22	16.14	30.08	110.48	7.26	20.26	5.58	13.92	36.68	8.18	45.44
Pr	1.46	1.34	0.38	2.12	22.94	0.36	4.02	0.52	1.28	4.66	1.06	10.18
Nd	13	6.08	3.38	8.74	98.18	3.32	24.68	5.02	16.46	38.52	9.34	72.26
Sm	6.44	4.76	4.48	6.24	27.8	2.46	3.86	2.88	8.26	9.7	5.06	13.82
Eu	0.38	0.24	0.54	0.52	1.08	0.114	0.144	0.38	0.32	0.96	0.116	0.162
Gd	31.5	24.66	40.02	44.74	81.64	20.32	17.78	17	56.56	45.88	25.72	48.24
Tb	9.34	8.3	12.5	15.14	20.38	5.62	4.7	4.9	14.14	13.04	8.42	10.48
Dy	126.7	50.9	65.16	73.32	91.14	100.32	67	71.32	175.26	147.88	103.88	160.3
Ho	58.32	44.66	53.84	65.32	74.94	34.08	19.46	23.14	68.84	51.94	37.14	75.34
Er	266	192.96	219.46	259.56	299.98	239.66	131.16	151.44	410.8	332.84	213.38	492.44
Tm	60.96	49.78	54.18	71.06	71.5	32.58	17.02	18.3	54.3	47.82	35.38	74.46
Yb	482.82	385.7	394.6	616.2	531.08	260.46	142.2	143.74	443.74	375.64	273.44	659.02
Lu	56	69.44	63.44	91.06	82.24	53.16	33.94	36.38	99.98	82.84	50.5	158.52
Hf	5521.02	7816.3	6322.22	8466.48	7013.54	5079.98	4488.38	3731.84	4303.02	7213.26	4848.3	9340.16
Ta	0.78	4.56	1.56	4.74	1.66	7.7	0.7	0.54	0.94	2.3	1.32	8.8
Pb206	72.66	94.68	60.22	110.78	57.1	46.84	13.52	9.16	24.32	276.04	63.62	191.92
Pb208	35.94	11.8	11.7	21.14	10.54	8.82	2.28	1.12	3.32	30.26	13.72	37.06
Th	212.76	252.54	200.46	419.02	266.16	61.18	18.56	14.08	48.3	127.9	92.36	176.08
U	136.02	157.5	90.42	202.18	142.48	46.4	16.08	6.78	28.74	95.74	37.14	189.98

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	AT-15C-EI-14	AT-15C-EI-15	AT-15C-EII-4b	AT-15C-EII-13	AT-15C-EII-15	AT-15C-EII-2	MAN-13A-AV3	MAN-13A-AV10	MAN-13A-AV6	MAN-13A-AV13
Pluton	Alto Turvo						Mandira			
Associação	Aluminosa						Alcalina			
Si	147617.41	147617.41	147617.39	147617.39	147617.39	147617.39	147617.38	147617.38	147617.36	147617.38
P	2582.05	1684.17	267.86	1075.27	226.66	239.96	231.88	313.57	149.67	318.15
Sc	302.39	240.15	266.12	212.37	311	254.79	173.69	130.23	136.01	147.7
Ti	<6.30	16.46	14.5	16220.03	31.26	17.94	186.74	72720.03	15.48	12.53
Mn	21.32	15.05	6.32	430.03	4.12	2.03	4.04	4099.95	1.14	<0.98
Sr	4.38	5.6	3.56	3.85	2.6	1.66	7.02	7.93	1.52	2.21
Y	1939.83	2033.11	2950.13	1692.89	2735.61	3039.27	6157.4	7144.59	3858.32	4529.54
Zr	697437.5	620806.75	619081.44	571427.5	651379.19	613000.5	453357.75	373219.59	299160.47	246241.11
Nb	55.51	55.05	56.98	162.44	42.14	46.09	62.43	415.34	69.66	60.09
Mo	46.79	46.61	51.4	43.47	42.9	39.87	22.89	18.63	21.27	15.44
Ba	0.76	10.05	8.23	3.81	8.67	1.69	1.96	1.81	0.34	1.9
La	87.24	41.68	15.21	12.34	2.65	0.84	41.36	152.66	1.36	544.15
Ce	249.62	149	79.89	61.56	52.1	31.09	232.19	561.99	74.42	1402.16
Pr	36.14	16.33	6.54	4.19	4.32	0.96	35.25	102.15	0.45	288.7
Nd	146.97	80.55	28.17	21.94	30.16	10.02	135.02	444.61	8.08	1423.46
Sm	41.38	33.74	18.01	8.48	27.09	16.94	50.29	148.63	10.79	384.41
Eu	1.9	2.88	0.65	0.72	3.25	0.86	0.51	1.74	0.4	3.94
Gd	61.62	71.9	59.95	33.03	87.37	84.78	181.59	252.37	87.4	620.82
Tb	18.76	18.7	17.86	10.62	26.38	29.22	66.47	57.65	24.57	101.63
Dy	188.09	203.01	283.04	123.38	278.52	283.07	688.36	741.81	287.3	798.73
Ho	60.88	68.3	100.95	47.71	93.94	92.77	204.62	184.3	136.99	187.48
Er	296.01	325.26	484.96	243.24	440.05	484.17	739.52	796.36	505.64	770.82
Tm	58.04	69.2	91.86	44.66	85.54	117.36	125.86	211.09	117.42	128.3
Yb	527.37	661.36	831.71	512.68	715.45	1158.41	1069.24	1801.94	990.9	976.26
Lu	121.7	120.58	127.92	99.66	124.45	185.26	214.68	228.44	135.61	129.94
Hf	17466.58	13671.42	13750.1	13352.9	13123.13	13383.75	9384.74	6920.81	5679.79	7376.15
Ta	3.76	3.44	3.72	8.54	1.62	1.8	3.67	16.86	8.91	6.56
Pb206	140.63	137.74	96.96	233.54	81.64	88.31	113.24	213.5	172.73	170.9
Pb208	17.68	18.26	18.68	31.33	13.78	16.35	30.29	61.58	26.78	27.83
Th	358.06	370.34	280.38	357.88	239.95	287.06	465.96	469.33	488.7	480.6
U	305.4	400.24	280.94	509.62	280.24	280.43	345.21	439.97	426.24	366.55

Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa

Amostra	AT-15C-EI-14	AT-15C-EI-15	AT-15C-EII-4b	AT-15C-EII-13	AT-15C-EII-15	AT-15C-EII-2	MAN-13A-AV3	MAN-13A-AV10	MAN-13A-AV6	MAN-13A-AV13
Pluton	Alto Turvo						Mandira			
	Erro 2 sigma (2σ)									
Si	9748.66	9554.8	9590.12	9526.28	9512.92	9554.08	9744.92	9725.7	9489.38	9726.72
P	3855.16	2688.86	491.54	2109.7	478.3	543.22	245.22	347.54	176.1	394.88
Sc	49.02	39.94	47.24	38.88	58.66	49.76	60.86	45.82	47.98	52.9
Ti	8.26	12.48	11.7	11040.46	23.38	14.7	85.92	31791.04	8.88	10.28
Mn	13.1	9.52	4.4	297.86	3.14	1.8	1.84	1387	0.88	1.2
Sr	1.22	1.5	1.06	1.14	0.8	0.56	2.74	3.12	0.64	0.98
Y	530.42	577.36	905.4	539.98	906.76	1046.74	2450.48	2888.44	1590.78	1912.7
Zr	306231.22	284749.5	310207.72	299252.1	356481.44	350515.18	200486.52	167203.04	136323.46	114614.74
Nb	16.86	17.26	19.24	56.64	15.28	17.32	26.14	174.78	29.72	26.16
Mo	19.38	19.64	23.26	20.32	20.74	20.04	8.64	7.18	7.74	6.24
Ba	0.68	3.9	3.48	1.76	3.8	0.94	1.2	1.16	0.3	1.18
La	23.28	11.5	4.52	3.78	0.86	0.32	10.04	37.46	0.38	139.78
Ce	63.34	38.92	22.2	17.62	15.36	9.46	53.82	131.76	17.78	341.3
Pr	11.78	5.5	2.38	1.58	1.68	0.42	14.88	43.26	0.22	125.52
Nd	74.66	42.18	15.88	12.72	17.9	6.28	82.66	273	5.18	897.7
Sm	8.64	6.94	4.2	2.14	6.1	4.14	19.22	56.34	4.3	150.1
Eu	0.78	1.02	0.32	0.32	1.24	0.4	0.34	0.82	0.22	1.76
Gd	23.7	28.1	25.2	14.42	38.88	39.08	43.22	60.44	21.38	153.8
Tb	6.26	6.4	6.56	4.04	10.3	11.8	18.12	15.98	6.94	29.4
Dy	81.4	90.98	136.64	61.86	144.66	152.5	190.72	207.72	81.64	231.44
Ho	28.84	33.48	53.16	26.04	53.08	54.3	71.54	65.04	48.94	68.22
Er	188.1	213.34	339.16	175.6	327.7	371.86	282.68	308.34	199.06	310.06
Tm	26.1	32.02	45.16	22.64	44.62	63.02	40.16	68.4	38.8	43.5
Yb	221.1	285.2	380.64	241.64	347.02	578.08	313.62	539.66	304.26	309.24
Lu	64.98	66.38	74.96	60.2	77.5	118.84	69.6	75.34	45.66	44.94
Hf	8281.24	6687.54	7161.14	7172.22	7267.06	7637.44	2795.8	2085	1736.38	2299.94
Ta	1.68	1.54	1.78	4.14	0.84	0.96	1.44	6.24	3.32	2.56
Pb206	60.74	61.48	46.58	115.9	42.04	47.12	46.38	87.8	71.82	72.58
Pb208	4.4	4.54	4.98	8.46	3.9	4.78	12.96	26.48	11.72	12.54
Th	59.54	63.04	50.46	66.06	45.52	55.94	142.54	145.88	154.84	156.1
U	44.2	59.08	43.7	81.08	45.76	46.98	83.94	108.64	107.2	94.56

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	MAN-13A-AV16	MAN-13A-AV12	MR-39BI-1	MR-39BI-2	MR-39BI-4	MR-39BI-5	MR-39BI-16	MR-39BII-2	MR-39BII-16	MR-39-BII-3	CO-32C-BIII-3	CO-32C-BIII-8
Pluton	Mandira					Papanduva						
Associação						Alcalina						
Si	147617.38	147617.38	147617.38	147617.36	147617.38	147617.38	147617.38	147617.38	147617.38	147617.38	148879.45	148879.45
P	240.29	1481.56	644.63	461.41	345.58	206.59	302.4	635.2	491.21	1011.51	410.01	169.68
Sc	254.66	180.64	177.62	184.75	206.84	100.46	159.9	295.37	226.82	212.57	242.61	154.37
Ti	20.95	468.13	130.07	127.14	99.06	28.77	214.37	31.67	37.38	41.1	6.52	4.15
Mn	1.73	22.01	5.93	10.26	<0.89	2.75	2.88	1.49	3.58	4.8	<1.16	<0.67
Sr	3.07	7.32	4.01	3.01	1.67	12.77	2.45	3.49	3.41	4.37	6.94	4.61
Y	6801.77	5828.56	3807.4	5536.04	4198.09	3216.66	4821.04	5286.56	4558.16	9427.59	23247.39	12363.42
Zr	558628.81	367938.84	414140.06	481555.94	527903.13	305889.53	416379.41	524490.38	529851.81	523177.78	651585.31	330845.25
Nb	110.41	34	119.42	112.99	55.9	82.25	58.84	67.43	85.76	187.08	112.8	71.88
Mo	38.94	23.12	27.35	30.45	31.25	20.98	30.07	52.83	42.24	38.76	36.94	25.97
Ba	0.95	2.87	8.23	3.56	<0.32	7.75	<0.21	4.03	1.46	7.14	<0.25	<0.073
La	6.69	968.05	364.59	86.72	17.73	67.16	156.71	27.07	32.7	12.5	0.216	0.461
Ce	109.43	1958.07	705.75	300.06	167.21	177.68	363.35	96.03	145.34	283.68	243.14	233.17
Pr	3.32	157.82	86.73	19.84	35.29	15	33.75	12.94	7.41	6.83	2.27	3.37
Nd	23.33	987.74	371.94	103.56	85.83	41.28	158.45	152.22	47.16	39.32	43.18	43.8
Sm	23.71	363.88	85.64	42.37	34.45	16.39	36.05	57.7	28.85	44.36	132.18	110.07
Eu	0.68	7.41	2.73	2.07	1.21	1.16	1.63	2.16	2.04	4.06	6.55	6.73
Gd	131.92	194.86	130.57	148.14	102.38	93.98	127.51	112.84	159.37	247.09	916.85	536.4
Tb	53.37	64.24	37.33	45.57	37.92	31.67	39.53	41.84	47.71	81.95	268.66	158.51
Dy	704.18	565.36	408.93	538.98	551.05	293.41	527.45	601.56	540.87	1132.03	2944.23	1701.42
Ho	277.61	162.64	113.91	173.15	196.14	104.21	168.11	267.8	132.41	352.81	668.77	415.26
Er	1284.16	710.84	431.1	780.85	646.61	416.25	656.93	1068.31	780.14	1332.47	2420.73	1375.88
Tm	217.97	150.41	72.41	129.79	85.43	80.15	113.11	115.9	165.13	214	368.14	213.49
Yb	1676.32	1165.61	639.86	1101.4	671.35	600.68	923.91	919.75	1130.5	1858.86	2532.26	1251.44
Lu	272.88	200.56	126.45	184.73	140.92	110.11	153.12	156.33	176.57	352.48	354.08	135.06
Hf	13430.86	8422.89	7142.61	6502.68	8174.4	4463.93	4762.13	6795.79	6900.26	8175.09	11473.05	7924.26
Ta	9.52	2.7	5.02	6.7	3.24	2.44	2.3	3.99	5.61	14.42	27.36	28.7
Pb206	196.49	148.25	143	172.89	82.56	34.63	92.93	166.87	161.32	367.27	179.69	119.87
Pb208	23.03	36.45	62.97	35.79	11.75	13.28	22	30.87	44.55	121.24	84.99	88.97
Th	399.93	281.86	571.91	655.23	218.65	173.47	381.83	282.18	698.33	2061.78	1746.38	1841.37
U	332.49	385.85	318.57	428.31	158.63	133.9	240.71	190.96	363.89	746.99	394.96	319.99

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	MAN-13A-AV16	MAN-13A-AV12	MR-39BI-1	MR-39BI-2	MR-39BI-4	MR-39BI-5	MR-39BI-16	MR-39BII-2	MR-39BII-16	MR-39-BII-3	CO-32C-BIII-3	CO-32C-BIII-8
Pluton	Mandira		Papanduva									
	Erro 2 sigma (2σ)											
Si	10067.82	10201.94	9565.62	10805.02	9607.8	9457.48	9779.38	9758.46	9712.14	9647.74	9600.26	9545.4
P	324.6	2084.48	1050.84	839.84	662.74	430.82	689.06	1575.8	1336.12	3018.26	445.74	184.96
Sc	92.64	67.1	68.16	73.38	83.04	41.28	67.46	127.36	100.16	96.06	89.5	57.24
Ti	17.02	227.64	66.18	76.02	53.84	16.5	121.32	21.58	24.64	26.94	4.98	3.44
Mn	1.82	9.1	2.7	6.3	1.02	1.48	1.94	1.62	2.4	3.02	1	0.64
Sr	1.44	3.32	1.9	1.7	0.88	6.62	1.4	2.02	2.04	2.7	3	2
Y	2950.9	2603.72	1811.16	2726.86	2137.34	1695.22	2631.42	2987.4	2666.12	5705.5	8726.72	4685.28
Zr	266437.82	180234	214969.6	258114.94	291796.04	174580.46	245479.6	319316.34	333030.84	339361.44	240241.88	123207.22
Nb	49.08	15.62	57	55.76	28.26	42.72	31.54	37.16	48.6	108.94	49.88	32.12
Mo	15.58	10.06	11.2	14.44	13.54	9.26	14.08	24.9	20.54	19.34	20.46	14.5
Ba	1.04	2	4.24	2.9	0.36	4.3	0.3	2.64	1.14	4.66	0.3	0.114
La	1.94	264.32	106.26	26.52	5.6	21.84	52.96	9.56	11.94	4.76	0.096	0.148
Ce	27.56	501.98	191.26	84.54	48.3	52.92	111.9	30.62	47.76	96.08	67.94	65.78
Pr	1.58	71.58	41.24	9.86	17.72	7.74	17.92	7.08	4.18	3.96	1.02	1.5
Nd	15.74	649.68	256.84	74.52	62.72	31	122.28	120.72	38.6	33.04	24.04	24.58
Sm	10.32	149.6	37.22	20.2	16.06	7.86	18	29.4	15.28	23.96	62.92	52.82
Eu	0.52	3.52	1.34	1.36	0.68	0.64	1	1.32	1.28	2.52	2.46	2.5
Gd	35.32	52.84	36.78	45.54	31.04	29.18	41.64	38.16	55.3	88.24	379.36	222.4
Tb	16.02	19.84	12.2	15.68	13.3	11.48	14.92	16.34	19.28	34.24	79.74	47.22
Dy	209.18	172.36	131.04	179.16	187.24	102.7	190.6	223.94	207.46	446.92	1018.76	590.86
Ho	103.2	61.94	45.56	71.48	82.92	45.32	75.34	123.46	62.82	172.08	154.84	96.7
Er	529.34	301.12	193.28	361.96	308.6	205.08	334.44	561.46	423.3	745.98	1180.8	675.98
Tm	76	54.08	27.7	51.62	35	33.98	49.74	52.8	77.88	104.48	169.42	98.78
Yb	548.88	395.64	233.44	420.08	265.38	247.14	396.68	411.54	527.02	902.66	1539.32	764.26
Lu	97.08	73.62	49.46	75.18	59.18	47.9	69.18	73.22	85.74	177.32	139.68	53.54
Hf	4284.74	2755.3	2463.58	2316.2	2991.08	1683.14	1852.4	2724.52	2850.82	3479.32	6914.42	4807.5
Ta	3.82	1.24	2.1	3.1	1.46	1.1	1.14	1.94	2.76	7.16	10.62	11.18
Pb206	85.5	66.24	66.68	83.84	40.84	17.64	48.8	89.86	89.36	208.88	62.58	41.92
Pb208	10.82	17.42	31.48	18.88	6.34	7.34	12.66	18.28	27.18	76.18	27.76	29.18
Th	133.66	97.1	209.24	248.76	85.7	70.36	160.54	122.88	314.7	961.58	542.74	573.4
U	88.34	105.52	92.46	129.28	49.32	43.06	80.28	65.96	130	276.1	74.26	60.42

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	CO-32C-BIII-10	CO-32C-BIII-16	CO-32C-BIV-3	CO-38-EI-5	CO-38-EI-15	CO-38-EI-16	CO-38-EII-8	CO-38-EII-16	CO-32D-CI-14	CO-32D-CI-10	CO-32D-CII-1	CO-32D-CII-4
Pluton	Corupá											
Associação							Alcalina					
Si	148879.45	148879.44	148879.44	148879.44	148879.44	148879.44	148879.44	148879.44	148879.44	148879.42	148879.41	148879.41
P	866.85	505.3	510.2	64.16	83.78	83.68	89.44	60.29	258.2	289.51	295.59	164.57
Sc	221.71	209.44	207.51	190.83	207.55	263.27	195.49	217.45	370.07	275.19	665.71	271.23
Ti	23.2	4.77	9.33	9.55	13.24	17.35	7.79	18.27	<3.69	10.19	4.16	6.27
Mn	<0.94	3.05	<0.79	<0.80	<0.81	<0.92	<0.86	<1.01	1.42	<0.76	16.84	41.57
Sr	11.82	7.14	10.4	0.66	0.94	1.17	0.91	0.78	3.98	3.89	5	3.02
Y	29155.76	19845.46	28103.42	1726.41	1864.75	3593.79	2027.7	1941.31	10396.41	11965.85	15274.92	9097.68
Zr	518219.28	471705.13	415862.78	458434.38	533534.06	650336.31	604648.13	641321	519978.28	594197.94	611038.81	544850.75
Nb	143.21	59.77	52.03	33.84	33.16	41.57	35.61	43.19	36.8	41.05	47.62	33.73
Mo	43.84	32.51	33.5	27.01	34.82	37.56	29.12	39.69	36.27	34.15	40.21	29.32
Ba	<0.204	0.22	<0.17	<0.156	<0.154	<0.185	<0.27	<0.30	0.157	<0.148	<0.188	0.53
La	0.306	1.11	2.1	0.13	0.71	0.193	0.054	0.065	0.55	0.384	0.67	0.348
Ce	639.54	279	394.28	27.72	31.03	30.15	23.56	29.71	168.23	119.48	320.3	119.53
Pr	2.72	2.37	5.25	0.52	0.59	1.24	0.43	0.42	2.67	2.83	8.1	2.1
Nd	51.87	37.09	83.74	7.96	7.36	23.31	5.96	8.01	44.94	47.76	144.87	36.63
Sm	146.99	102.18	216.6	12.39	9.44	27.28	9.97	12	61.13	79.32	218.46	62.37
Eu	8.38	5.83	10.03	0.191	0.146	0.216	0.35	0.326	10.79	4.44	28.21	9.34
Gd	1056.63	595.96	1246.16	55.78	52.62	113.83	53.83	56.29	304.93	365.04	895.41	338.84
Tb	298.1	193.79	442.75	15.84	15.51	28.84	14.93	14.05	89.58	105.58	238.53	95.2
Dy	3535.79	2661.35	4465.09	197.58	183.71	354.18	199.88	186.15	1143.77	1309.36	2338.02	990.95
Ho	1108.05	747.59	895.43	67.18	53.35	107.92	64.44	62.64	360.98	447.16	552.52	305.94
Er	4162.36	3153.01	2835.94	324.08	226.7	495.28	246.46	289.77	1649.48	1919	1954.71	1233.51
Tm	676.98	619.92	403.59	63.02	48.67	102.86	42.91	56.36	306.42	316.45	366.55	235.95
Yb	4720.31	4532.94	2429.22	502.51	408.18	874.74	385.63	487.47	2765.38	2217.03	3024.13	1835.26
Lu	701.19	661.87	287.16	90.63	81.06	149.03	65.62	95.45	593.11	351.25	464.85	295.25
Hf	7021.73	6799.35	9131.47	6381.74	7381.87	6392.71	6166.81	8464.97	8275.86	7599.29	6924.89	6987.2
Ta	10.2	2.51	14.09	0.82	0.86	0.64	0.69	0.75	2	1.17	2.09	1.66
Pb206	392.74	157.86	158.04	22.2	18.7	17.75	20.08	16.8	76.92	198.72	135.36	69.6
Pb208	265.74	49.48	112.47	4.84	4.53	5.57	6.13	2.97	18.7	85.72	28.02	10.08
Th	6488.96	1145.84	2338.75	98.14	107.09	108.7	117.31	60.59	472.41	2176.34	636.15	177.92
U	1125.3	474.27	437.34	55.87	50.31	47.71	52.69	43.41	227.86	641.74	366.62	166.58

**Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa**

Amostra	CO-32C-BIII-10	CO-32C-BIII-16	CO-32C-BIV-3	CO-38-EI-5	CO-38-EI-15	CO-38-EI-16	CO-38-EII-8	CO-38-EII-16	CO-32D-CI-14	CO-32D-CI-10	CO-32D-CII-1	CO-32D-CII-4
Pluton	Corupá											
	Erro 2 sigma (2σ)											
Si	9579.74	9659.3	9622.14	9550.1	9529	9559.12	9544.8	9563.06	9558.18	9527.44	9573.22	9778.3
P	942.9	553.22	562.78	75.58	98.74	100.74	108.82	76.82	341.32	390.32	406.96	233.14
Sc	82.84	79.16	79.4	76.76	85.16	110.36	83.82	95.42	179.06	136.54	338.64	141.66
Ti	13.32	5.18	6.58	6.66	8.38	11.18	5.9	12.32	4.24	8.08	4.84	7.72
Mn	0.84	1.06	0.8	0.72	0.7	0.8	0.74	0.84	0.82	0.66	3.24	7.98
Sr	5.14	3.18	4.66	0.34	0.48	0.6	0.48	0.42	2.3	2.3	3.04	1.92
Y	11186.74	7730.1	11137.76	729.58	807.74	1597.66	926.1	911.7	5485.24	6503.52	8552.92	5248.34
Zr	195480.64	180711.3	162160.56	190806.6	227687.6	284936.5	272256.22	297030.12	270988.12	319136.16	338251.26	310889.38
Nb	64.8	27.52	24.38	16.94	17.02	21.9	19.28	24.06	23.1	26.54	31.74	23.24
Mo	24.64	18.66	19.44	16.54	21.74	24.02	19.1	26.68	27.12	26.2	31.72	24
Ba	0.19	0.28	0.22	0.192	0.156	0.168	0.2	0.24	0.166	0.134	0.166	0.6
La	0.116	0.36	0.62	0.06	0.24	0.086	0.038	0.044	0.22	0.156	0.28	0.186
Ce	182.68	80.98	116.4	8.76	10.04	10.02	8.04	10.42	66.14	48.4	133.66	51.46
Pr	1.22	1.1	2.4	0.26	0.3	0.64	0.24	0.24	1.58	1.72	5.02	1.38
Nd	29.48	21.56	49.14	5.1	4.82	15.46	4.14	5.7	35.24	38.58	120.42	31.64
Sm	71.3	50.4	108.24	6.7	5.22	15.3	5.8	7.16	40.16	53.54	151.62	44.78
Eu	3.14	2.26	3.82	0.126	0.1	0.146	0.188	0.186	5	2.12	13.62	4.7
Gd	440.02	250.4	528.32	24.9	23.88	52.48	25.42	27.14	159.64	195.4	490.18	190.14
Tb	89.34	58.66	135.44	5.12	5.1	9.64	5.12	4.92	34.24	41.32	95.58	39.14
Dy	1235.94	939.22	1594.12	74.12	70.24	138.14	79.7	75.92	511.92	600.28	1098.06	477.04
Ho	260.28	177.72	215.72	17.1	13.86	28.64	17.52	17.44	111	141.06	178.9	101.76
Er	2065.64	1584.94	1447.28	175.28	125.42	280.56	143.14	172.66	1094.12	1308.24	1369.68	888.46
Tm	315.78	292.4	192.94	31.78	25.06	54.14	23.14	31.12	187.02	198.18	235.54	155.6
Yb	2904.16	2817.84	1529.54	332.98	276.02	604.34	272.56	352.7	2207.16	1814.46	2537.94	1579.48
Lu	279.88	266.92	117.3	38.94	35.52	66.72	30.04	44.72	306.24	185.94	252.28	164.34
Hf	4300.6	4215.34	5743.7	4244.2	5017.78	4447.1	4394.72	6185.02	6715.02	6333.24	5927.92	6143.66
Ta	4.04	1.06	5.72	0.38	0.4	0.32	0.34	0.38	1.06	0.64	1.16	0.98
Pb206	138.02	56.24	56.92	8.5	7.3	7.1	8.18	7.02	34.82	91.96	64.26	34.08
Pb208	87.74	16.64	38.12	1.78	1.7	2.14	2.38	1.22	8.1	37.82	12.74	4.82
Th	2031.02	361.64	745.68	32.74	36.36	37.64	41.44	21.88	186.28	877.82	262.58	75.24
U	213.92	91.18	85.08	11.46	10.5	10.18	11.48	9.68	55.54	160.14	93.78	43.8

Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa

Amostra	CO-32D-CII-12	CO-32D-CII-13	CO-32D-CI-1	MR-254-CII-8	MR-254-CII-5	MR-254-CII-4	MR-254-CII-11	MR-254-CI-15	MR-254-CI-14
Pluton	Corupá			Riolito Associado - Complexo Morro Redondo					
Associação	Alcalina								
Si	148879.42	148879.41	148879.42	147617.34	147617.34	147617.34	147617.34	147617.34	147617.34
P	308.48	207.47	737.78	389.79	433.51	402.15	293.37	402.48	292.11
Sc	711.91	256.47	267.99	325.3	246.74	328.89	328.2	303.78	282.1
Ti	7.02	13.46	3.69	8.46	<3.76	6.1	2.85	4.23	<4.38
Mn	1.37	<1.04	<0.81	1.32	<0.99	<0.94	<0.80	<1.26	2.56
Sr	5.3	2.77	7.52	1.2	3.44	2.26	2.54	1.93	1.53
Y	16140.29	7882.26	20749.22	2475.82	7650.25	4731.88	6538.1	3901.44	4236.98
Zr	643541.19	626986.56	575233.56	544863.38	581476.56	640775.75	617323.75	509739.31	774793.69
Nb	39.9	43.78	71.29	57.14	51.42	73.13	56.24	75.59	92.93
Mo	34.97	45.87	40.08	47.73	39.7	46.91	48.8	48.77	62.57
Ba	0.68	<0.216	<0.175	<0.22	<0.160	0.29	0.27	<0.25	0.24
La	0.95	0.5	0.388	0.237	0.107	1.58	1.22	0.97	0.213
Ce	420.69	79.63	285.2	35.79	50.27	65.78	47.74	54.36	49.87
Pr	10.61	2.05	2.32	0.197	0.77	0.52	0.88	0.51	0.44
Nd	196.41	30.64	39.91	2.92	10.83	5.39	11.65	7.64	7.31
Sm	295.94	51.8	85.83	8.57	21.26	11.12	21.83	19.32	13.37
Eu	38.17	2.36	7.2	0.088	0.49	0.259	0.175	0.32	0.26
Gd	999.97	201.42	474.14	51.81	149.56	72.05	128.27	107.06	73.67
Tb	223.15	63.97	155.44	20.92	50.26	30.55	52.99	32.49	29.85
Dy	1943.83	826.27	2154.52	268.8	654.34	373.28	779.38	360.49	481.41
Ho	519.6	302.63	715.75	103.63	225.54	142.69	247.36	151.79	207.54
Er	2173.36	1363.63	3068.74	409.4	1021.74	630.15	927.96	668.32	896.16
Tm	419.31	248.94	546.05	95.15	193.47	135.14	149.16	140.41	167.35
Yb	3633.69	2117.45	4255.89	869.17	1681.88	1102.84	1373.19	1085.21	1223.95
Lu	523.61	316.8	628.95	165.27	297.24	226.29	223.95	180.16	213.47
Hf	7480.29	8264.89	9681.1	16454.48	13432.55	17582.22	14890.41	13900.28	16514.73
Ta	1.07	1.41	6.01	5.81	5.51	6.97	3.72	6.04	5.83
Pb206	69.91	136.37	134.09	137.52	213.28	193.34	193.64	204.34	170.57
Pb208	35.17	38.54	24.4	24.5	45.07	42.44	44.03	49.79	34.62
Th	902.06	672.33	709.51	565.01	1087.24	1128.54	889.68	1326.98	920.18
U	222.26	273.42	586.72	388.23	521.16	610.14	517.58	519.81	444.54

Tabela 12: Análises químicas de elementos-traços por LA-ICP-MS em cristais de zircão de diversos plútons graníticos e sieníticos e riolito da
Província Graciosa

Amostra	CO-32D-CII-12	CO-32D-CII-13	CO-32D-CI-1	MR-254-CII-8	MR-254-CII-5	MR-254-CII-4	MR-254-CII-11	MR-254-CI-15	MR-254-CI-14
Pluton	Corupá								
	Riolito Associado - Complexo Morro Redondo								
	Erro 2 sigma (2σ)								
Si	9610.02	9616.04	9541.96	9518.1	9512.74	9563.96	9723.72	9761.88	9749.18
P	442.48	304.3	1100.28	1169.32	1184.5	1020.16	702.02	918.06	641.86
Sc	380.72	140.66	150.58	110.3	85.6	117.36	121.18	116.34	112.3
Ti	6.7	11.88	4.14	6.84	3.86	6.4	4.62	5.72	6.34
Mn	0.9	0.96	0.68	0.98	0.84	0.9	1	1.36	1.36
Sr	3.4	1.84	5.04	0.24	0.5	0.4	0.52	0.46	0.38
Y	9589.46	4822.86	13070.98	367.94	1161.58	738.36	1053.68	650.88	733.14
Zr	378362.66	379820.26	358959.04	224398.18	244345.06	276347.9	274535.26	234544	369755.6
Nb	28.28	31.98	53.6	23.3	21.46	31.44	25.06	34.94	44.66
Mo	29.16	39.24	35.16	23.14	19.72	23.98	25.98	26.92	35.68
Ba	0.58	0.2	0.136	0.22	0.178	0.36	0.36	0.32	0.36
La	0.4	0.24	0.18	0.096	0.062	0.42	0.38	0.34	0.124
Ce	186.38	36.38	134.06	8.9	12.8	17.3	13.1	15.5	14.84
Pr	6.94	1.4	1.6	0.108	0.34	0.26	0.46	0.3	0.28
Nd	173.4	28	37.46	1.18	3.76	2.14	4.64	3.4	3.38
Sm	217.34	39.24	66.7	2.92	7	3.94	7.92	7.34	5.42
Eu	19.28	1.26	3.82	0.084	0.24	0.17	0.174	0.24	0.22
Gd	572.72	118.14	283.88	21.84	64.54	32.42	60.06	52.48	37.96
Tb	93.76	27.54	68.42	8.26	20.3	12.76	22.92	14.64	14.04
Dy	957.82	416.98	1112.76	42.58	105.34	62	133.52	64.36	88.84
Ho	177.16	105.88	256.7	35.3	78.86	51.56	92.74	59.28	84.54
Er	1608.26	1036.72	2396.14	132.44	339.14	216	329.92	247.3	345.76
Tm	283.58	172.68	388.34	38.3	79.96	57.74	66.18	64.88	80.7
Yb	3205.4	1914.5	3942.7	293.2	583.42	395.96	512.62	422.58	498.08
Lu	298.6	185.16	376.54	49.58	91.28	71.6	73.38	61.3	75.56
Hf	6753.92	7661.88	9212.4	6021.7	5035.92	6791.32	5953.82	5771.96	7138.78
Ta	0.64	0.86	3.64	2.86	2.78	3.62	2.06	3.42	3.44
Pb206	34.92	69.62	70.04	62.46	99.82	93.9	98.12	108.24	94.74
Pb208	16.8	18.86	12.24	10.24	19.26	18.74	20.22	23.78	17.28
Th	389.64	297.02	320.44	193.14	378.98	403.6	328.06	506	363.8
U	59.72	75.22	165.16	114.76	156.82	188.02	164.18	170.22	150.64

Tabela 13: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons sieníticos e graníticos de tipo-A e riolito associado da associação alcalina da Província Graciosa

Ponto	²⁰⁶ Pb cps	²³⁸ U cps	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb idade (Ma)	2σ	²⁰⁶ Pb/ ²³⁸ U idade (Ma)	2σ	Discórdia (%)
Plúton Corupá: amostra CO-32C														
BIII - 1	1980	261639	0.0584	0.0012	0.7750	0.0335	0.0961	0.0037	0.8692	543.5	±47	591.7	±23	-8.9
BIII - 2	46916	363572	0.0578	0.0013	0.7632	0.0321	0.0956	0.0035	0.8433	521.5	±50	588.8	±22	-12.9
BIII - 3	67661	507921	0.0593	0.0012	0.7995	0.0332	0.0976	0.0037	0.8707	579.6	±45	600.3	±23	-3.6
BIII - 4	82048	623508	0.0610	0.0011	0.8234	0.0370	0.0978	0.0041	0.9092	639.7	±40	601.3	±25	6.0
BIII - 5	12080	92877	0.0609	0.0023	0.7941	0.0438	0.0945	0.0039	0.7331	636.6	±81	581.8	±24	8.6
BIII - 6	46392	349601	0.0575	0.0015	0.7647	0.0388	0.0964	0.0043	0.8499	510.6	±59	593.3	±26	-16.2
BIII - 7	91149	644087	0.0694	0.0032	0.9615	0.0537	0.1004	0.0032	0.5493	910.6	±96	617.0	±20	32.2
BIII - 8	71456	544094	0.0601	0.0011	0.7851	0.0301	0.0948	0.0033	0.8679	605.6	±41	583.9	±20	3.6
BIII - 9	104789	753719	0.0594	0.0011	0.8109	0.0301	0.0990	0.0034	0.8792	581.7	±39	608.8	±21	-4.6
BIII - 10	88855	669966	0.0595	0.0011	0.7881	0.0302	0.0960	0.0034	0.8847	587.0	±39	591.2	±21	-0.7
BIII - 12	62971	484251	0.0608	0.0013	0.7884	0.0338	0.0941	0.0036	0.8579	633.3	±48	579.7	±22	8.5
BIII - 13	58208	445006	0.0588	0.0011	0.7511	0.0348	0.0928	0.0040	0.9085	559.3	±42	571.9	±25	-2.3
BIII - 14	58541	448138	0.0568	0.0012	0.7300	0.0305	0.0933	0.0034	0.8508	484.5	±49	575.1	±21	-18.7
BIII - 15	113453	868835	0.0585	0.0009	0.7514	0.0262	0.0934	0.0031	0.8943	546.7	±34	575.6	±19	-5.3
BIII - 16	57964	448465	0.0596	0.0012	0.7634	0.0301	0.0930	0.0033	0.8704	590.1	±42	573.5	±20	2.8
BIV - 1	50320	382847	0.0575	0.0013	0.7433	0.0305	0.0935	0.0034	0.8490	511.5	±48	576.2	±21	-12.6
BIV - 2	71187	537923	0.0597	0.0015	0.7795	0.0367	0.0945	0.0039	0.8547	591.8	±53	582.3	±24	1.6
BIV - 3	57624	437067	0.0597	0.0011	0.7906	0.0318	0.0960	0.0036	0.8956	591.0	±39	590.7	±22	0.1
BIV - 4	60490	451076	0.0592	0.0010	0.7758	0.0309	0.0949	0.0036	0.9135	574.5	±35	584.5	±22	-1.7
BIV - 5	9362	69614	0.0579	0.0018	0.7507	0.0367	0.0939	0.0037	0.7831	526.8	±67	578.6	±23	-9.8
BIV - 6	30633	238059	0.0607	0.0015	0.7722	0.0317	0.0923	0.0032	0.8005	627.5	±53	568.8	±20	9.3
BIV - 7	24969	187970	0.0575	0.0018	0.7709	0.0451	0.0973	0.0049	0.8455	509.5	±69	598.3	±30	-17.4
BIV - 8	13169	99165	0.0591	0.0022	0.7900	0.0419	0.0970	0.0037	0.6990	570.6	±82	596.5	±23	-4.5
Plúton Corupa: Amostra CO-32D														
CI -1	90423	680456	0.0590	0.0010	0.7580	0.0315	0.0928	0.0036	0.9108	565.5	±37	572.0	±22	-1.2
CI -4	167054	1266526	0.0607	0.0012	0.7940	0.0308	0.0946	0.0033	0.8620	629.2	±43	582.5	±20	7.4
CI -5	90368	721342	0.0581	0.0013	0.7252	0.0313	0.0903	0.0035	0.8676	535.4	±47	557.1	±22	-4.1
CI -6	14508	111719	0.0639	0.0026	0.8173	0.0442	0.0927	0.0035	0.6680	737.0	±85	571.4	±21	22.5
CI -7	11704	90106	0.0606	0.0024	0.7535	0.0423	0.0902	0.0038	0.7207	623.8	±84	556.5	±23	10.8
CI -8	6996	53486	0.0573	0.0043	0.7382	0.0628	0.0934	0.0040	0.4899	504.7	±163	575.4	±25	-14.0
CI -9	72911	552424	0.0599	0.0013	0.7848	0.0316	0.0951	0.0034	0.8436	599.0	±47	585.8	±21	2.2
CI -10	73979	556983	0.0588	0.0020	0.7565	0.0348	0.0934	0.0031	0.6927	561.3	±72	575.4	±19	-2.5
CI -11	32264	248027	0.0594	0.0016	0.7608	0.0341	0.0932	0.0034	0.7923	580.0	±59	574.2	±21	1.0
CI -14	25846	199609	0.0604	0.0018	0.7792	0.0371	0.0939	0.0036	0.7738	618.4	±65	578.7	±22	6.4
CI -15	41801	318940	0.0587	0.0012	0.7355	0.0326	0.0913	0.0037	0.8867	555.9	±45	563.3	±23	-1.3
CI -16	41801	318940	0.0601	0.0013	0.7665	0.0326	0.0931	0.0035	0.8567	606.1	±48	573.6	±22	5.4
CII -1	49914	519716	0.0592	0.0013	0.7618	0.0295	0.0935	0.0031	0.8281	576.1	±47	576.2	±19	0.0
CII -3	12711	135017	0.0618	0.0025	0.7752	0.0421	0.0912	0.0034	0.6683	666.4	±87	562.4	±21	15.6

Tabela 13: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons sieníticos e graníticos de tipo-A e riolito associado da associação alcalina da Província Graciosa

Ponto	²⁰⁶ Pb cps	²³⁸ U cps	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb idade (Ma)	2σ	²⁰⁶ Pb/ ²³⁸ U idade (Ma)	2σ	Discórdia (%)
Plúton Corupa: Amostra CO-32D														
CII -4	37287	384580	0.0593	0.0027	0.7802	0.0433	0.0955	0.0032	0.5771	578.4	±99	588.2	±20	-1.7
CII -5	13265	142663	0.0621	0.0023	0.7767	0.0404	0.0907	0.0034	0.7035	679.0	±79	559.8	±21	17.5
CII -6	21659	226243	0.0610	0.0025	0.7827	0.0407	0.0931	0.0032	0.6360	640.0	±86	573.7	±20	10.4
CII -7	22246	234328	0.0598	0.0016	0.7588	0.0351	0.0920	0.0036	0.8144	597.3	±58	567.2	±22	5.0
CII -8	23446	247108	0.0630	0.0015	0.8232	0.0384	0.0948	0.0039	0.8635	706.7	±50	583.8	±24	17.4
CII -9	21429	218409	0.0605	0.0013	0.8146	0.0342	0.0975	0.0037	0.8638	621.9	±46	600.0	±23	3.5
CII -11	18941	199336	0.0604	0.0017	0.7667	0.0330	0.0918	0.0032	0.7685	619.4	±60	566.3	±20	8.6
CII -12	34671	362402	0.0586	0.0015	0.7575	0.0314	0.0935	0.0031	0.7726	552.1	±58	576.4	±19	-4.4
CII -13	62386	655281	0.0597	0.0012	0.7611	0.0295	0.0923	0.0032	0.8456	591.6	±45	568.9	±20	3.8
CII -14	21112	222185	0.0615	0.0019	0.7126	0.0388	0.0958	0.0044	0.8248	655.3	±66	589.7	±27	10.0
Plúton Corupá: Amostra CO-38														
EI -1	10257	111753	0.0620	0.0029	0.7765	0.0449	0.0910	0.0032	0.5780	674.4	±101	561.3	±20	16.8
EI -2	7462	78704	0.0637	0.0023	0.8061	0.0408	0.0920	0.0034	0.7036	730.4	±76	567.2	±21	22.3
EI -3	4820	52524	0.0609	0.0035	0.7638	0.0522	0.0911	0.0035	0.5363	634.3	±124	562.2	±21	11.4
EI -4	9795	102508	0.0796	0.0070	1.0842	0.1038	0.0989	0.0039	0.3976	1186.3	±174	608.1	±24	48.7
EI -5	10105	106905	0.0604	0.0023	0.7779	0.0397	0.0935	0.0034	0.6827	617.6	±81	576.1	±21	6.7
EI -6	9277	95953	0.0581	0.0021	0.7661	0.0382	0.0957	0.0034	0.6892	532.9	±79	589.1	±21	-10.5
EI -7	6299	65620	0.0551	0.0028	0.7126	0.0451	0.0938	0.0037	0.6060	415.7	±112	578.2	±23	-39.1
EI -8	7754	54645	0.3407	0.0548	6.7217	1.1748	0.1431	0.0099	0.3922	3665.8	±246	862.1	±60	76.5
EI -9	8398	61328	0.3202	0.0192	5.8844	0.4825	0.1332	0.0076	0.6833	3570.7	±92	806.4	±46	77.4
EI -10	86491	887671	0.0708	0.0039	0.9464	0.0653	0.0969	0.0041	0.5951	950.8	±114	596.4	±25	37.3
EI -11	69172	727338	0.0613	0.0014	0.8017	0.0308	0.0948	0.0030	0.7933	648.9	±50	583.9	±19	10.0
EI -12	7373	76606	0.0606	0.0023	0.8003	0.0434	0.0956	0.0038	0.7062	626.2	±83	588.7	±23	6.0
EI -13	4191	44294	0.0619	0.0049	0.7933	0.0691	0.0929	0.0034	0.4104	669.6	±170	572.5	±21	14.5
EI -14	8945	95420	0.0626	0.0021	0.7867	0.0368	0.0911	0.0031	0.6861	693.4	±73	561.8	±19	19.0
EI -15	5393	56616	0.0604	0.0035	0.7916	0.0562	0.0948	0.0039	0.5681	619.4	±126	584.0	±24	5.7
EI -16	6660	69367	0.0590	0.0027	0.7801	0.0455	0.0958	0.0036	0.6195	565.7	±100	589.5	±22	-4.2
EII -1	9833	106912	0.0605	0.0027	0.7718	0.0423	0.0930	0.0032	0.5966	619.9	±95	573.4	±20	7.5
EII -2	5867	64180	0.0561	0.0027	0.7091	0.0434	0.0920	0.0037	0.6317	458.3	±105	567.1	±23	-23.7
EII -3	6422	69013	0.0612	0.0033	0.7993	0.0512	0.0951	0.0034	0.5439	645.5	±115	585.4	±21	9.3
EII -4	7568	67688	0.2216	0.0511	3.6964	0.9350	0.1213	0.0127	0.4126	2992.7	±371	737.8	±77	75.3
EII -5	9455	100805	0.0568	0.0024	0.7411	0.0432	0.0949	0.0039	0.6752	482.1	±95	584.4	±24	-21.2
EII -6	19599	205893	0.0570	0.0018	0.7453	0.0377	0.0950	0.0039	0.7856	491.1	±69	584.8	±24	-19.1
EII -7	8006	83669	0.0751	0.0109	0.9715	0.1493	0.0939	0.0046	0.3144	1069.9	±293	578.8	±29	45.9
EII -8	6453	70243	0.0586	0.0024	0.7402	0.0412	0.0916	0.0036	0.6734	551.5	±90	565.1	±22	-2.5
EII -9	6514	70761	0.0774	0.0041	0.9960	0.0639	0.0933	0.0035	0.5597	1130.2	±106	575.1	±21	49.1
EII -10	6775	72621	0.0984	0.0036	1.2259	0.0634	0.0902	0.0034	0.7078	1594.2	±68	556.8	±21	65.1
EII -11	10730	114539	0.0628	0.0030	0.8110	0.0494	0.0935	0.0036	0.6170	701.0	±102	576.2	±22	17.8

Tabela 13: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons sieníticos e graníticos de tipo-A e riolito associado da associação alcalina da Província Graciosa

Ponto	²⁰⁶ Pb cps	²³⁸ U cps	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb idade (Ma)	2σ	²⁰⁶ Pb/ ²³⁸ U idade (Ma)	2σ	Discórdia (%)
Plúton Corupá: Amostra CO-38														
EII -12	3472	39009	0.0628	0.0046	0.7857	0.0655	0.0905	0.0038	0.4918	702.3	±154	558.3	±24	20.5
EII -13	7292	78247	0.0619	0.0035	0.8149	0.0561	0.0951	0.0038	0.5552	671.6	±123	585.7	±23	12.8
EII -14	4873	53505	0.0607	0.0041	0.8084	0.0647	0.0962	0.0043	0.5463	628.8	±144	592.1	±27	5.8
EII -15	15244	168372	0.0662	0.0026	0.8377	0.0434	0.0914	0.0031	0.6370	812.5	±83	563.5	±19	30.6
EII -16	5218	57859	0.0591	0.0039	0.7403	0.0606	0.0904	0.0044	0.5813	569.7	±145	558.0	±27	2.1
Plúton Mandira: MAN-13A														
CV-1	142360	1241645	0.0909	0.0019	1.0863	0.0420	0.0867	0.0030	0.8430	1443.6	±40	536.1	±18	62.9
CV-2	45690	379376	0.0599	0.0014	0.7703	0.0319	0.0932	0.0033	0.8199	600.5	±51	574.7	±20	4.3
CV-3	39983	329657	0.0626	0.0014	0.7960	0.0320	0.0923	0.0032	0.8241	693.3	±49	569.0	±20	17.9
CV-4	186817	1424983	0.1916	0.0212	2.5774	0.3181	0.0976	0.0055	0.4455	2755.6	±181	600.2	±34	78.2
CV-5	41779	343912	0.0617	0.0014	0.7877	0.0314	0.0926	0.0032	0.8324	662.8	±47	571.1	±20	13.8
CV-6	75493	628153	0.0627	0.0015	0.7839	0.0324	0.0906	0.0032	0.8252	698.9	±50	559.3	±20	20.0
CV-8	68641	591171	0.0706	0.0012	0.8499	0.0319	0.0873	0.0030	0.8890	946.0	±35	539.5	±19	43.0
CV-9	46977	388651	0.0603	0.0009	0.7617	0.0277	0.0916	0.0032	0.9204	614.0	±31	565.1	±20	8.0
CV-10	48913	409169	0.0607	0.0019	0.7226	0.0413	0.0864	0.0042	0.8281	628.1	±69	533.9	±26	15.0
CV-11	25460	207559	0.0589	0.0020	0.7545	0.0412	0.0930	0.0041	0.7866	561.7	±74	573.1	±25	-2.0
CV-12	51689	416331	0.0597	0.0010	0.7613	0.0268	0.0925	0.0030	0.8778	592.4	±37	570.2	±18	3.7
CV-13	64320	526558	0.0608	0.0015	0.7684	0.0325	0.0917	0.0033	0.8244	631.9	±52	565.3	±20	10.5
CV-14	15344	128037	0.0601	0.0020	0.7280	0.0358	0.0878	0.0033	0.7363	607.2	±72	542.7	±20	10.6
CV-15	16116	133321	0.0630	0.0018	0.7838	0.0402	0.0903	0.0039	0.8266	706.9	±62	557.1	±24	21.2
CV-16	41117	321838	0.0618	0.0016	0.7762	0.0357	0.0911	0.0036	0.8212	665.7	±56	562.3	±22	15.5
Plúton Papanduva (Complexo Morro Redondo): Amostra MR-39														
BI-1	22191	247320	0.0992	0.0073	1.2990	0.1060	0.0949	0.0035	0.4401	1609.8	±137	584.5	±22	63.7
BI-2	51699	599194	0.0733	0.0013	0.9309	0.0327	0.0921	0.0029	0.8552	1021.9	±37	568.0	±18	44.4
BI-3	5693	63569	0.0554	0.0022	0.7251	0.0369	0.0949	0.0032	0.6337	428.9	±88	584.4	±20	-36.3
BI-4	5693	63569	0.0554	0.0022	0.7264	0.0370	0.0951	0.0032	0.6335	428.9	±88	585.4	±20	-36.5
BI-5	10587	121369	0.0589	0.0018	0.7619	0.0346	0.0939	0.0033	0.7522	562.4	±65	578.3	±21	-2.8
BI-6	8734	104693	0.0641	0.0028	0.7894	0.0446	0.0893	0.0034	0.6459	746.0	±91	551.2	±21	26.1
BI-7	11970	118067	0.1691	0.0113	2.6177	0.1988	0.1123	0.0042	0.4706	2549.0	±112	685.8	±25	73.1
BI-8	16268	174603	0.0867	0.0088	1.2004	0.1297	0.1004	0.0039	0.3432	1354.0	±196	616.8	±24	54.4
BI-9	25142	264765	0.0762	0.0079	1.0632	0.1195	0.1012	0.0045	0.3828	1100.6	±208	621.3	±27	43.5
BI-10	4269	333356	0.1408	0.0238	1.9035	0.3281	0.0981	0.0033	0.1863	2236.9	±293	603.0	±20	73.0
BI-11	13660	83516	0.4688	0.0546	10.8133	1.6360	0.1673	0.0163	0.6390	4146.1	±172	997.1	±97	76.0
BI-12	18667	217113	0.0677	0.0024	0.8659	0.0401	0.0927	0.0030	0.6563	860.7	±73	571.6	±18	33.6
BI-13	15446	178306	0.0626	0.0020	0.8173	0.0363	0.0946	0.0031	0.7038	696.3	±67	582.8	±19	16.3
BI-14	13496	156258	0.0574	0.0017	0.7418	0.0317	0.0937	0.0030	0.7240	507.0	±65	577.6	±19	-13.9
BI-15	12946	146786	0.0755	0.0036	0.9783	0.0570	0.0940	0.0033	0.5701	1081.7	±96	579.1	±20	46.5
BI-16	22774	267938	0.0597	0.0023	0.7589	0.0375	0.0923	0.0031	0.6411	591.2	±82	569.0	±19	3.8

Tabela 13: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons sieníticos e graníticos de tipo-A e riolito associado da associação alcalina da Província Graciosa

Ponto	²⁰⁶ Pb cps	²³⁸ U cps	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb idade (Ma)	2σ	²⁰⁶ Pb/ ²³⁸ U idade (Ma)	2σ	Discórdia (%)
Plúton Papanduva (Complexo Morro Redondo): Amostra MR-39														
BII-1	32181	273222	0.0671	0.0015	0.8786	0.0415	0.0949	0.0040	0.8755	841.9	±48	584.5	±25	30.6
BII-2	23307	195509	0.0600	0.0017	0.7889	0.0347	0.0953	0.0034	0.7804	604.7	±60	586.8	±21	3.0
BII-3	146868	1230630	0.0603	0.0010	0.7940	0.0286	0.0955	0.0032	0.8965	613.4	±35	588.2	±20	4.1
BII-4	13227	114002	0.0755	0.0035	0.9498	0.0609	0.0912	0.0041	0.6860	1082.6	±94	562.6	±25	48.0
BII-5	63778	535969	0.0739	0.0058	0.9664	0.0832	0.0949	0.0035	0.4089	1037.7	±159	584.4	±21	43.7
BII-6	40494	341727	0.0625	0.0016	0.8116	0.0340	0.0942	0.0033	0.7924	690.2	±55	580.4	±20	15.9
BII-7	53894	454005	0.0663	0.0019	0.8588	0.0380	0.0939	0.0033	0.7708	816.1	±59	578.7	±21	29.1
BII-8	52586	451169	0.0760	0.0068	0.9460	0.0893	0.0902	0.0029	0.3224	1096.2	±179	556.8	±18	49.2
BII-9	16689	144514	0.0622	0.0026	0.7851	0.0426	0.0916	0.0033	0.6425	680.4	±89	564.8	±20	17.0
BII-10	46864	384754	0.0634	0.0016	0.7777	0.0343	0.0890	0.0033	0.8124	721.5	±55	549.4	±20	23.9
BII-11	22870	196953	0.0599	0.0015	0.7427	0.0323	0.0900	0.0034	0.8254	598.2	±53	555.5	±21	7.1
BII-12	20691	176937	0.0612	0.0019	0.7774	0.0356	0.0921	0.0032	0.7235	645.8	±68	568.2	±20	12.0
BII-13	12106	103974	0.0628	0.0037	0.7708	0.0563	0.0890	0.0040	0.5971	701.4	±125	549.7	±25	21.6
BII-14	26306	205727	0.1115	0.0106	1.4856	0.1510	0.0966	0.0037	0.3638	1824.0	±172	594.6	±23	67.4
BII-15	26830	224407	0.0704	0.0028	0.8844	0.0491	0.0911	0.0037	0.7008	941.1	±81	561.8	±23	40.3
BII-16	33292	284144	0.0603	0.0018	0.7428	0.0333	0.0893	0.0031	0.7433	615.4	±65	551.4	±19	10.4
BII - 17	46536	352405	0.0611	0.0013	0.7870	0.0351	0.0941	0.0038	0.8863	644.1	±44	579.8	±24	10.0
BII - 18	45022	330264	0.0652	0.0055	0.8553	0.0807	0.0957	0.0041	0.4422	780.2	±178	589.3	±25	24.5
BII - 19	67123	489305	0.0787	0.0023	1.0432	0.0474	0.0957	0.0034	0.7596	1165.5	±59	588.9	±21	49.5
BII - 20	25037	189747	0.0603	0.0019	0.7569	0.0396	0.0904	0.0039	0.8003	614.3	±68	558.0	±24	9.2
BII - 21	27418	201597	0.0645	0.0016	0.8540	0.0383	0.0953	0.0037	0.8372	756.5	±52	587.0	±23	22.4
Complexo Morro Redondo - riolito: Amostra MR-254														
CI - 1	81525	404611	0.3452	0.0061	6.6524	0.3318	0.1394	0.0067	0.9363	3686.0	±27	841.3	±40	77.2
CI - 2	74768	440708	0.2613	0.0073	4.2385	0.2574	0.1174	0.0064	0.8879	3254.6	±44	715.5	±39	78.0
CI - 3	186882	357903	0.7385	0.0089	36.0912	1.2222	0.3538	0.0117	0.9356	4807.6	±17	1952.5	±65	59.4
CI - 4	48508	111455	0.6736	0.0275	28.2180	3.4807	0.3034	0.0354	0.9436	4675.4	±59	1707.9	±200	63.5
CI - 5	75288	476444	0.2088	0.0037	3.0770	0.1180	0.1068	0.0038	0.8886	2896.3	±29	653.9	±23	77.4
CI - 6	45325	200812	0.4485	0.0082	9.5561	0.3805	0.1544	0.0057	0.8892	4080.3	±27	925.6	±34	77.3
CI - 7	43709	210237	0.3732	0.0058	7.4266	0.3415	0.1443	0.0064	0.9423	3804.3	±23	868.8	±39	77.2
CI - 8	73097	276659	0.5090	0.0056	12.5783	0.5179	0.1792	0.0073	0.9636	4267.4	±16	1062.7	±43	75.1
CI - 9	64004	325329	0.3294	0.0069	5.9842	0.2487	0.1318	0.0049	0.8631	3614.3	±32	798.1	±30	77.9
CI - 10	216666	569795	0.6718	0.0335	28.1224	4.0579	0.3038	0.0412	0.9383	4671.5	±72	1710.3	±232	63.4
CI - 11	39043	287878	0.0590	0.0010	0.7570	0.0328	0.0932	0.0038	0.9156	565.5	±38	574.6	±24	-1.6
CI - 12	62666	469425	0.0599	0.0014	0.7471	0.0308	0.0906	0.0032	0.8269	598.9	±50	559.3	±20	6.6
CI - 13	79722	600458	0.0599	0.0009	0.7423	0.0280	0.0900	0.0032	0.9135	600.3	±33	555.7	±20	7.4
CI - 14	48366	348415	0.0582	0.0010	0.7633	0.0354	0.0954	0.0042	0.9229	535.9	±39	587.3	±26	-9.6
CI - 15	63157	451292	0.0600	0.0014	0.8000	0.0343	0.0969	0.0037	0.8495	604.6	±49	596.2	±22	1.4
CI - 16	60924	442365	0.0601	0.0012	0.7657	0.0346	0.0927	0.0038	0.8914	606.4	±44	571.5	±24	5.8

Tabela 13: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons sieníticos e graníticos de tipo-A e riolito associado da associação alcalina da Província Graciosa

Ponto	²⁰⁶ Pb cps	²³⁸ U cps	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb idade (Ma)	2σ	²⁰⁶ Pb/ ²³⁸ U idade (Ma)	2σ	Discórdia (%)
Complexo Morro Redondo - riolito: Amostra MR-254														
CII - 1	77747	553200	0.0589	0.0010	0.7712	0.0300	0.0953	0.0035	0.8982	564.6	±37	586.6	±21	-3.9
CII - 2	46922	346529	0.0601	0.0012	0.7715	0.0344	0.0934	0.0038	0.8978	607.0	±43	575.7	±24	5.2
CII - 3	113808	784923	0.0580	0.0009	0.7911	0.0321	0.0991	0.0038	0.9234	530.9	±34	609.3	±24	-14.8
CII - 4	59157	429558	0.0588	0.0011	0.7612	0.0313	0.0941	0.0035	0.8817	560.1	±42	579.6	±22	-3.5
CII - 5	89658	632740	0.0596	0.0009	0.7888	0.0321	0.0962	0.0038	0.9346	588.3	±32	592.0	±23	-0.6
CII - 6	59637	427002	0.0589	0.0013	0.7774	0.0334	0.0958	0.0036	0.8481	563.9	±50	589.8	±22	-4.6
CII - 7	81402	582986	0.0599	0.0010	0.7840	0.0298	0.0950	0.0034	0.8937	599.8	±37	584.9	±21	2.5
CII - 8	47371	333694	0.0595	0.0012	0.7962	0.0343	0.0971	0.0038	0.8877	585.3	±43	597.1	±24	-2.0
CII - 9	207715	1599500	0.0631	0.0013	0.7621	0.0324	0.0875	0.0034	0.8725	712.7	±44	540.7	±21	24.1
CII - 10	46518	360150	0.0693	0.0033	0.8540	0.0606	0.0892	0.0048	0.7466	908.6	±97	551.0	±30	39.4
CII - 11	77386	553868	0.0596	0.0010	0.7884	0.0295	0.0957	0.0034	0.9048	590.3	±35	589.4	±21	0.2
CII - 12	60716	434639	0.0607	0.0012	0.7931	0.0319	0.0945	0.0034	0.8695	628.8	±43	582.4	±21	7.4
CII - 13	49926	358070	0.0610	0.0014	0.7986	0.0349	0.0947	0.0037	0.8587	639.9	±48	583.1	±23	8.9
CII - 14	37890	276845	0.0608	0.0021	0.7974	0.0518	0.0948	0.0053	0.8401	632.0	±76	584.0	±32	7.6
CII - 15	59506	424551	0.0593	0.0012	0.7881	0.0320	0.0961	0.0035	0.8768	577.5	±42	591.3	±22	-2.4
CII - 16	91429	679244	0.0605	0.0011	0.7689	0.0302	0.0917	0.0033	0.8803	622.4	±40	565.8	±20	9.1

Tabela 14: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons graníticos de tipo-A da associação aluminosa da Província Graciosa

Ponto	^{206}Pb cps	^{238}U cps	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ idade (Ma)	2σ	$^{206}\text{Pb}/^{238}\text{U}$ idade (Ma)	2σ	Discórdia (%)
Plúton Alto Turvo: Amostra AT-15C														
EI - 1	25902	288007	0.3579	0.0490	5.5906	0.8178	0.1143	0.0060	0.3540	3740.9	±208	697.9	±37	81.3
EI - 2	21804	316502	0.1159	0.0371	1.3344	0.4301	0.0841	0.0030	0.1079	1894.0	±576	520.8	±19	72.5
EI - 3	154264	2018586	0.0637	0.0011	0.7774	0.0272	0.0890	0.0028	0.8646	733.3	±37	549.7	±17	25.0
EI - 4	86971	1371043	0.0760	0.0032	0.7817	0.0445	0.0749	0.0029	0.6662	1096.2	±85	465.7	±18	57.5
EI - 5	81516	1094896	0.0643	0.0011	0.7949	0.0302	0.0900	0.0032	0.8951	750.9	±36	555.5	±20	26.0
EI - 6	24540	190633	0.5148	0.0960	13.1843	2.7006	0.1861	0.0159	0.4136	4284.1	±274	1100.5	±94	74.3
EI - 7	101080	1010045	0.3862	0.0223	6.5068	0.4460	0.1223	0.0047	0.5396	3856.1	±87	743.8	±28	80.7
EI - 8	5729	59223	0.1154	0.0420	1.6283	0.6099	0.1023	0.0090	0.2327	1886.3	±656	627.7	±55	66.7
EI - 9	9232	121755	0.0629	0.0028	0.8064	0.0432	0.0928	0.0030	0.5739	705.8	±93	571.9	±18	19.0
EI - 10	36709	432916	0.3358	0.0189	4.7297	0.3053	0.1018	0.0034	0.4934	3643.6	±86	625.2	±21	82.8
EI - 11	39884	475969	0.0651	0.0026	0.9285	0.0487	0.1030	0.0036	0.6428	777.9	±85	631.7	±22	18.8
EI - 12	65758	799146	0.0708	0.0028	0.9690	0.0499	0.0988	0.0033	0.6301	950.4	±82	607.1	±21	36.1
EI - 13	116475	568793	0.1586	0.0043	5.2531	0.3658	0.2385	0.0155	0.9201	2441.0	±46	1379.0	±89	43.5
EI - 14	38227	504694	0.0587	0.0015	0.7759	0.0346	0.0951	0.0036	0.8081	555.6	±57	585.6	±22	-5.4
EI - 15	20661	288080	0.0581	0.0019	0.7487	0.0345	0.0925	0.0031	0.7031	534.7	±72	570.5	±19	-6.7
EI - 16	22670	369155	0.1085	0.0043	1.2079	0.0795	0.0799	0.0043	0.8025	1774.9	±72	495.3	±27	72.1
EII - 1	21672	301960	0.0806	0.0045	1.0187	0.0673	0.0922	0.0033	0.5196	1212.0	±111	568.4	±20	53.1
EII - 2	22310	308970	0.0611	0.0019	0.7732	0.0364	0.0922	0.0033	0.7370	643.2	±68	568.6	±21	11.6
EII - 3	25108	347777	0.0575	0.0019	0.7364	0.0336	0.0933	0.0031	0.6947	510.5	±72	574.8	±19	-12.6
EII - 4	13905	184947	0.0611	0.0039	0.8153	0.0581	0.0970	0.0032	0.4434	643.7	±137	597.0	±20	7.3
EII - 5	23671	306111	0.0613	0.0030	0.8671	0.0535	0.1029	0.0039	0.5948	648.3	±107	631.3	±24	2.6
EII - 6	14597	218204	0.1205	0.0098	1.3866	0.1365	0.0836	0.0047	0.5682	1963.4	±145	517.5	±29	73.6
EII - 7	51584	719738	0.0730	0.0033	0.9396	0.0517	0.0935	0.0030	0.5580	1012.6	±93	576.0	±19	43.1
EII - 8	10670	146176	0.0609	0.0024	0.8222	0.0445	0.0979	0.0038	0.6948	636.3	±84	601.8	±23	5.4
EII - 9	65427	1116972	0.0764	0.0019	0.8179	0.0340	0.0775	0.0027	0.8076	1106.1	±49	481.4	±17	56.5
EII - 10	12510	149102	0.0786	0.0020	1.2369	0.0583	0.1139	0.0046	0.8346	1162.1	±52	695.5	±28	40.2
EII - 11	44029	600597	0.0671	0.0016	0.8976	0.0349	0.0967	0.0031	0.7783	842.4	±51	595.0	±19	29.4
EII - 12	22839	316219	0.0598	0.0017	0.7954	0.0346	0.0961	0.0033	0.7655	596.3	±61	591.7	±21	0.8
EII - 13	36040	497610	0.0734	0.0067	0.9862	0.0963	0.0970	0.0034	0.3430	1026.1	±186	596.7	±21	41.9
EII - 14	12844	245651	0.0710	0.0019	0.6907	0.0314	0.0702	0.0027	0.8166	958.4	±54	437.1	±17	54.4
EII - 15	12051	170539	0.0594	0.0018	0.8005	0.0344	0.0972	0.0031	0.7118	580.2	±66	598.2	±19	-3.1
EII - 16	17775	243907	0.0619	0.0016	0.8366	0.0355	0.0974	0.0034	0.8000	670.1	±55	599.1	±21	10.6
Plúton Guaraú: Amostra GUA-16														
DI-1 - 1	420768	2392053	0.3048	0.0082	4.8989	0.2098	0.1166	0.0041	0.7784	3494.6	±42	710.9	±25	79.7
DI-1 - 2	306677	1780925	0.2676	0.0040	4.4182	0.1826	0.1197	0.0048	0.9344	3292.1	±23	729.1	±29	77.9
DI-1 - 3	253408	1756730	0.2800	0.0088	3.6839	0.2040	0.0954	0.0045	0.8230	3363.0	±49	587.5	±27	82.5
DI-1 - 4	24534	176371	0.0586	0.0019	0.7677	0.0401	0.0950	0.0040	0.7922	551.5	±70	585.3	±25	-6.1
DI-1 - 5	16493	120340	0.0649	0.0024	0.8147	0.0443	0.0911	0.0038	0.7400	770.9	±77	561.8	±23	27.1

Tabela 14: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons graníticos de tipo-A da associação aluminosa da Província Graciosa

Ponto	^{206}Pb cps	^{238}U cps	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ idade (Ma)	2σ	$^{206}\text{Pb}/^{238}\text{U}$ idade (Ma)	2σ	Discórdia (%)
Plúton Guaraú: Amostra GUA-16														
DI-1 - 6	42368	311353	0.0596	0.0012	0.7608	0.0328	0.0927	0.0037	0.8898	587.3	±43	571.3	±23	2.7
DI-1 - 7	7019	50285	0.0637	0.0025	0.8189	0.0495	0.0932	0.0044	0.7543	731.6	±84	574.7	±27	21.4
DI-1 - 8	18784	141510	0.0607	0.0016	0.7724	0.0444	0.0924	0.0048	0.8824	627.2	±58	569.5	±29	9.2
DI-1 - 9	962640	5469032	0.1184	0.0043	1.8498	0.1782	0.1133	0.0102	0.9269	1932.1	±65	692.0	±62	64.2
DI-1 - 10	1204798	6096049	0.0825	0.0052	1.4850	0.1169	0.1305	0.0062	0.5933	1257.8	±124	790.9	±38	37.1
DI-1 - 11	442263	512649	0.2183	0.0025	17.7608	0.7200	0.5900	0.0237	0.9605	2968.5	±18	2989.4	±120	-0.7
DI-1 - 12	32868	247204	0.0605	0.0013	0.7320	0.0309	0.0878	0.0033	0.8526	621.7	±48	542.2	±20	12.8
DI-1 - 13	18188	125484	0.0607	0.0018	0.8012	0.0446	0.0957	0.0046	0.8425	629.1	±65	589.2	±28	6.3
DI-1 - 14	43176	286144	0.0898	0.0108	1.2610	0.1617	0.1018	0.0047	0.3513	1421.3	±229	625.2	±29	56.0
DI-1 - 15	47238	330513	0.0611	0.0016	0.8183	0.0381	0.0971	0.0039	0.8341	644.3	±55	597.2	±24	7.3
DI-1 - 16	21630	167818	0.0660	0.0018	0.7715	0.0380	0.0847	0.0036	0.8290	807.3	±58	524.4	±22	35.0
DI-2 - 17	12085	88035	0.0609	0.0023	0.7675	0.0403	0.0913	0.0034	0.6888	634.6	±82	563.0	±21	11.3
DI-2 - 18	12085	88035	0.0730	0.0052	0.8984	0.0768	0.0891	0.0044	0.5628	1013.5	±143	550.3	±27	45.7
DI-2 - 19	28132	207819	0.2404	0.0061	3.6251	0.2037	0.1092	0.0056	0.8921	3122.8	±40	668.1	±34	78.6
DI-2 - 20	298376	2313003	0.3472	0.0130	4.0628	0.3393	0.0848	0.0064	0.8939	3694.7	±57	524.6	±40	85.8
DI-2 - 21	80345	520780	0.3008	0.0082	4.4971	0.2237	0.1083	0.0046	0.8391	3474.6	±42	663.0	±28	80.9
DI-2 - 22	11414	84332	0.0625	0.0030	0.7711	0.0482	0.0894	0.0038	0.6543	692.0	±101	551.9	±23	20.2
DI-2 - 23	1705594	11404302	0.0628	0.0018	0.8785	0.0507	0.1014	0.0052	0.8721	701.1	±60	622.8	±32	11.2
DI-2 - 24	1658817	11081398	0.0588	0.0006	0.8053	0.0268	0.0994	0.0033	0.9480	558.5	±23	610.8	±20	-9.4
DI-2 - 25	835319	6750299	0.0680	0.0010	0.7783	0.0284	0.0830	0.0029	0.9196	868.6	±30	514.2	±18	40.8
DI-2 - 26	741904	4860349	0.1559	0.0025	2.0699	0.1250	0.0963	0.0057	0.9628	2412.1	±28	592.9	±35	75.4
Plúton Quiriri (Complexo Morro Redondo): Amostra MR-161														
BI-1	24886	264665	0.0598	0.0016	0.6965	0.0298	0.0849	0.0029	0.7725	595.0	±59	525.2	±18	11.7
BI-2	37689	407266	0.0618	0.0013	0.7222	0.0271	0.0851	0.0028	0.8274	666.7	±45	526.4	±17	21.0
BI-3	20177	216136	0.0620	0.0027	0.7308	0.0400	0.0858	0.0030	0.6205	672.8	±92	530.6	±19	21.1
BI-4	38093	399861	0.0618	0.0016	0.7503	0.0303	0.0882	0.0029	0.7698	668.5	±55	544.9	±18	18.5
BI-5	16433	177695	0.0630	0.0027	0.7398	0.0402	0.0852	0.0030	0.6232	709.8	±90	527.3	±19	25.7
BI-6	32390	342169	0.0595	0.0013	0.7305	0.0291	0.0891	0.0031	0.8293	586.3	±48	550.2	±19	6.2
BI-7	50356	580308	0.0824	0.0034	0.9284	0.0471	0.0818	0.0026	0.5937	1254.3	±80	506.7	±16	59.6
BI-8	51777	588498	0.0739	0.0045	0.8626	0.0648	0.0846	0.0038	0.5806	1039.4	±123	523.5	±23	49.6
BI-9	30211	327041	0.0598	0.0022	0.7319	0.0347	0.0886	0.0029	0.6531	598.2	±78	547.3	±18	8.5
BI-10	112612	1139261	0.0835	0.0284	1.0185	0.3485	0.0884	0.0034	0.1079	1280.2	±663	545.8	±21	57.4
BI-11	71472	756552	0.0599	0.0009	0.7580	0.0262	0.0915	0.0030	0.9021	601.1	±32	564.5	±18	6.1
BI-12	27439	290350	0.0586	0.0020	0.7447	0.0353	0.0919	0.0031	0.6795	553.3	±76	566.5	±19	-2.4
BI-13	38766	401199	0.0606	0.0015	0.7896	0.0312	0.0942	0.0030	0.7743	624.1	±54	580.4	±19	7.0
BI-14	25098	261886	0.0612	0.0016	0.8036	0.0335	0.0948	0.0032	0.7860	646.6	±55	584.1	±20	9.7
BI-15	32804	339427	0.0640	0.0019	0.8569	0.0374	0.0966	0.0033	0.7459	743.0	±61	594.5	±20	20.0
BI-16	30746	328368	0.0610	0.0014	0.7930	0.0336	0.0939	0.0035	0.8472	637.5	±49	578.4	±22	9.3

Tabela 14: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons graníticos de tipo-A da associação aluminosa da Província Graciosa

Ponto	^{206}Pb cps	^{238}U cps	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ idade (Ma)	2σ	$^{206}\text{Pb}/^{238}\text{U}$ idade (Ma)	2σ	Discórdia (%)
Plúton Quiriri (Complexo Morro Redondo): Amostra MR-161														
BII-1	31176	325558	0.0669	0.0026	0.8875	0.0472	0.0960	0.0036	0.6803	835.6	±81	591.2	±22	29.2
BII-2	50258	523622	0.0588	0.0020	0.7727	0.0400	0.0952	0.0038	0.7534	559.8	±74	586.2	±24	-4.7
BII-3	31890	339677	0.0599	0.0022	0.7810	0.0423	0.0945	0.0039	0.7349	599.9	±80	582.0	±24	3.0
BII-4	48208	514146	0.0626	0.0016	0.8177	0.0352	0.0947	0.0034	0.7964	694.8	±56	583.0	±21	16.1
BII-5	29161	314973	0.0639	0.0015	0.8310	0.0359	0.0942	0.0035	0.8349	739.1	±50	580.5	±22	21.5
BII-6	28134	288175	0.0627	0.0018	0.8175	0.0353	0.0946	0.0032	0.7603	696.8	±60	582.5	±20	16.4
BII-7	29380	296548	0.1038	0.0070	1.4642	0.1133	0.1023	0.0041	0.4988	1693.4	±124	627.6	±25	62.9
BII-8	36444	386049	0.0599	0.0017	0.7642	0.0371	0.0925	0.0038	0.8197	599.5	±60	570.6	±23	4.8
BII-9	24865	258052	0.0594	0.0022	0.7983	0.0419	0.0974	0.0037	0.6948	583.4	±82	599.2	±23	-2.7
BII-10	24787	267183	0.0616	0.0012	0.7563	0.0311	0.0891	0.0033	0.8750	659.6	±43	550.1	±21	16.6
BII-11	27602	289803	0.0603	0.0022	0.7942	0.0424	0.0956	0.0038	0.7290	614.3	±79	588.3	±24	4.2
BII-12	36990	383390	0.0569	0.0019	0.7550	0.0372	0.0963	0.0036	0.7243	487.2	±75	592.7	±22	-21.7
BII-13	37530	411639	0.0604	0.0011	0.7620	0.0320	0.0916	0.0036	0.8949	616.9	±41	565.1	±22	8.4
BII-14	24893	273257	0.0600	0.0018	0.7405	0.0325	0.0896	0.0031	0.7457	604.2	±63	553.0	±19	8.5
BII-15	37056	386832	0.0591	0.0013	0.7883	0.0346	0.0968	0.0038	0.8639	570.9	±48	595.8	±23	-4.4
BII-16	45650	488001	0.0603	0.0011	0.7656	0.0309	0.0922	0.0034	0.8848	613.5	±41	568.7	±21	7.3
Plúton Quiriri (Complexo Morro Redondo): Amostra MR-186A														
CI-1	14081	155705	0.0613	0.0019	0.7597	0.0329	0.0905	0.0029	0.7151	648.9	±65	558.6	±18	13.9
CI-2	32781	360489	0.0578	0.0010	0.7198	0.0250	0.0908	0.0029	0.8710	524.1	±38	560.0	±18	-6.9
CI-3	15350	167850	0.0609	0.0018	0.7641	0.0322	0.0914	0.0030	0.7299	635.5	±62	564.0	±18	11.3
CI-4	24330	263103	0.0600	0.0018	0.7735	0.0336	0.0938	0.0031	0.7219	605.2	±65	577.8	±19	4.5
CI-5	12286	139512	0.0639	0.0034	0.7892	0.0498	0.0898	0.0031	0.5218	739.5	±114	554.1	±19	25.1
CI-6	26979	299761	0.0590	0.0019	0.7390	0.0336	0.0911	0.0031	0.7207	565.6	±69	561.8	±19	0.7
CI-7	16287	181576	0.0593	0.0023	0.7450	0.0375	0.0912	0.0031	0.6431	577.7	±84	562.7	±19	2.6
CI-8	32570	355402	0.0612	0.0013	0.7867	0.0305	0.0933	0.0032	0.8380	645.3	±46	574.8	±19	10.9
CI-9	20398	218623	0.0605	0.0021	0.8069	0.0369	0.0967	0.0030	0.6542	619.9	±75	595.0	±19	4.0
CI-10	32839	362362	0.0579	0.0024	0.7352	0.0400	0.0919	0.0033	0.6431	526.2	±91	566.7	±21	-7.7
CI-11	17167	187348	0.0579	0.0019	0.7438	0.0359	0.0929	0.0034	0.7280	524.7	±73	572.8	±21	-9.2
CI-12	28606	311265	0.0593	0.0016	0.7815	0.0347	0.0953	0.0035	0.7929	576.5	±59	586.6	±21	-1.7
CI-13	16267	177898	0.0595	0.0019	0.7850	0.0357	0.0952	0.0032	0.7052	585.9	±70	586.2	±20	0.0
CI-14	21085	225319	0.0641	0.0019	0.8634	0.0390	0.0971	0.0034	0.7540	744.7	±63	597.5	±21	19.8
CI-15	21597	239122	0.0684	0.0024	0.8908	0.0424	0.0938	0.0032	0.6904	881.3	±71	577.8	±20	34.4
CI-16	33923	379531	0.0581	0.0016	0.7622	0.0313	0.0944	0.0031	0.7554	533.3	±59	581.6	±19	-9.1
CII-1	20152	227160	0.0587	0.0017	0.7651	0.0312	0.0936	0.0029	0.7163	555.9	±62	576.8	±18	-3.8
CII-2	47794	543329	0.0607	0.0012	0.7835	0.0281	0.0928	0.0030	0.8445	628.9	±41	572.2	±18	9.0
CII-3	21848	249101	0.0576	0.0015	0.7432	0.0301	0.0929	0.0031	0.7828	515.8	±55	572.6	±19	-11.0
CII-4	18205	200658	0.0597	0.0021	0.7959	0.0373	0.0961	0.0031	0.6579	594.0	±77	591.5	±19	0.4
CII-5	16394	175819	0.0589	0.0017	0.7666	0.0338	0.0940	0.0033	0.7581	564.1	±63	579.0	±20	-2.6

Tabela 14: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons graníticos de tipo-A da associação aluminosa da Província Graciosa

Ponto	^{206}Pb cps	^{238}U cps	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$ idade (Ma)	2σ	$^{206}\text{Pb}/^{238}\text{U}$ idade (Ma)	2σ	Discórdia (%)
Plúton Quiriri (Complexo Morro Redondo): Amostra MR-186A														
CII-6	17498	190855	0.0590	0.0062	0.7902	0.0869	0.0968	0.0033	0.2950	568.8	±229	595.6	±20	-4.7
CII-7	16287	181576	0.0591	0.0023	0.7708	0.0387	0.0945	0.0032	0.6389	570.3	±84	582.0	±20	-2.1
CII-8	21389	242467	0.0759	0.0019	0.9885	0.0434	0.0944	0.0035	0.8163	1093.5	±51	581.6	±22	46.8
CII-9	31202	354852	0.0582	0.0014	0.7455	0.0304	0.0930	0.0032	0.8064	538.0	±53	573.3	±20	-6.6
CII-10	25954	284823	0.0580	0.0019	0.7548	0.0368	0.0947	0.0035	0.7391	529.0	±72	583.3	±22	-10.3
CII-11	35472	393732	0.0595	0.0013	0.7697	0.0285	0.0943	0.0030	0.8182	584.6	±46	580.7	±18	0.7
CII-12	12830	146184	0.0584	0.0021	0.7551	0.0385	0.0943	0.0036	0.7171	544.7	±78	581.0	±22	-6.7
CII-13	14728	164959	0.0624	0.0025	0.8179	0.0414	0.0957	0.0032	0.6252	688.6	±84	589.2	±20	14.4
CII-14	26085	290387	0.0620	0.0017	0.8079	0.0338	0.0953	0.0031	0.7444	674.9	±60	586.7	±19	13.1
CII-15	38618	437354	0.0635	0.0030	0.8034	0.0492	0.0926	0.0037	0.6229	725.9	±102	571.1	±23	21.3
CII-16	42824	496211	0.0600	0.0012	0.7802	0.0311	0.0954	0.0034	0.8551	604.1	±45	587.1	±21	2.8
Plúton Quiriri (Complexo Morro Redondo): Amostra MR-201A														
AI - 1	25939	198244	0.0571	0.0015	0.7502	0.0372	0.0956	0.0041	0.8378	494.0	±60	588.8	±25	-19.2
AI - 2	31727	228430	0.0586	0.0014	0.8135	0.0382	0.1010	0.0042	0.8569	550.8	±53	620.4	±26	-12.6
AI - 3	46813	365050	0.0575	0.0015	0.7419	0.0318	0.0937	0.0034	0.8057	512.2	±56	577.5	±21	-12.7
AI - 4	42116	327755	0.0579	0.0012	0.7378	0.0294	0.0926	0.0033	0.8657	526.0	±44	570.8	±20	-8.5
AI - 5	42581	327878	0.0713	0.0020	0.9417	0.0496	0.0959	0.0044	0.8477	965.7	±57	590.6	±27	38.8
AI - 6	65620	493424	0.0600	0.0014	0.7976	0.0361	0.0964	0.0039	0.8646	605.1	±49	593.4	±24	1.9
AI - 7	30962	242618	0.0580	0.0015	0.7502	0.0338	0.0939	0.0036	0.8255	528.2	±56	578.7	±22	-9.6
AI - 8	114471	885144	0.0607	0.0012	0.7810	0.0340	0.0934	0.0038	0.8990	627.5	±41	575.4	±23	8.3
AI - 9	84545	1058101	0.2099	0.0047	1.7176	0.0805	0.0593	0.0025	0.8777	2904.7	±36	371.5	±16	87.2
AI - 10	58551	454452	0.0597	0.0011	0.7658	0.0312	0.0930	0.0035	0.8863	592.3	±41	573.0	±21	3.3
AI - 11	33511	250278	0.0957	0.0135	1.3093	0.1915	0.0991	0.0039	0.2579	1542.5	±266	608.9	±24	60.5
AI - 12	26971	203406	0.0587	0.0037	0.7742	0.0633	0.0954	0.0050	0.6277	557.7	±139	587.4	±31	-5.3
AI - 13	34246	305749	0.0649	0.0020	0.7225	0.0315	0.0805	0.0026	0.7089	772.3	±65	499.2	±16	35.4
AI - 14	65871	521201	0.0596	0.0012	0.7586	0.0307	0.0920	0.0034	0.8690	589.6	±43	567.6	±21	3.7
AI - 15	34262	272557	0.0576	0.0014	0.7336	0.0312	0.0921	0.0034	0.8342	514.0	±52	568.0	±21	-10.5
AI - 16	30534	237090	0.0594	0.0014	0.7707	0.0339	0.0937	0.0036	0.8327	583.0	±53	577.5	±22	0.9
AII - 1	27825	216301	0.0602	0.0013	0.7640	0.0316	0.0922	0.0034	0.8615	612.3	±45	568.8	±21	7.1
AII - 2	25780	196809	0.0595	0.0016	0.7665	0.0360	0.0936	0.0037	0.8098	586.1	±60	577.0	±23	1.6
AII - 3	29450	220775	0.0614	0.0015	0.8185	0.0389	0.0969	0.0040	0.8515	653.0	±54	596.2	±25	8.7
AII - 4	95938	911862	0.1021	0.0034	1.0565	0.0489	0.0752	0.0025	0.6858	1663.0	±62	467.2	±16	71.9
AII - 5	202128	2852650	0.3986	0.0087	2.8010	0.1248	0.0510	0.0020	0.8726	3904.0	±33	320.8	±13	91.8
AII - 6	24468	188410	0.0703	0.0028	0.9121	0.0516	0.0942	0.0039	0.7163	936.6	±81	580.3	±24	38.0
AII - 7	43086	347022	0.0641	0.0019	0.7935	0.0365	0.0897	0.0032	0.7566	746.6	±64	554.1	±20	25.8
AII - 8	29318	228624	0.0624	0.0016	0.7842	0.0329	0.0912	0.0032	0.7929	687.4	±55	562.4	±20	18.2
AII - 9	62480	483472	0.0587	0.0014	0.7504	0.0318	0.0927	0.0034	0.8304	554.9	±52	571.6	±21	-3.0
AII - 10	37034	266575	0.0618	0.0012	0.8239	0.0472	0.0966	0.0053	0.9455	667.8	±40	594.4	±33	11.0

Tabela 14: Determinações geocronológicas U-Pb (LA-ICP-MS) em cristais de zircão de plútons graníticos de tipo-A da associação aluminosa da Província Graciosa

Ponto	²⁰⁶ Pb cps	²³⁸ U cps	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb idade (Ma)	2σ	²⁰⁶ Pb/ ²³⁸ U idade (Ma)	2σ	Discórdia (%)
Plúton Quiriri (Complexo Morro Redondo): Amostra MR-201A														
All - 11	41694	316459	0.0600	0.0020	0.7835	0.0395	0.0946	0.0037	0.7611	603.4	±71	582.7	±23	3.4
All - 12	40754	321586	0.0605	0.0015	0.7527	0.0363	0.0901	0.0038	0.8477	620.8	±55	556.2	±23	10.4
All - 13	87766	687101	0.0592	0.0009	0.7391	0.0258	0.0904	0.0030	0.9062	573.4	±32	557.9	±19	2.7
All - 14	38790	304854	0.0596	0.0014	0.7387	0.0303	0.0897	0.0031	0.8066	588.1	±53	553.8	±19	5.8
All - 15	67926	510407	0.0613	0.0011	0.8011	0.0324	0.0945	0.0036	0.8994	650.6	±38	581.9	±22	10.6
All - 16	43454	310231	0.0594	0.0013	0.8111	0.0381	0.0986	0.0042	0.8805	582.9	±48	606.5	±26	-4.0

Tabela 15: Razões isotópicas Lu-Hf (LA-MC-ICP-MS) em cristais de zircão do Complexo Morro Redondo

Amostra/Análise	$^{176}\text{Hf}/^{177}\text{Hf}$ medido	2σ	$^{176}\text{Lu}/^{177}\text{Hf}$ medido	2σ	t (Ma)	$^{176}\text{Hf}/^{177}\text{Hf}$ (i)	$\varepsilon\text{Hf}(0)$	f(Lu/Hf)	$\varepsilon\text{Hf}(t)$	$T_{\text{DM}}(1)$
Plúton Papanduva										
MR-39 BI-LH-2	0.28192	0.00022	0.00225	0.0000495	5.80E+08	0.28190	-30.1	-0.932	-18.2	1.9E+09
MR-39 BI-LH-3	0.28202	0.00005	0.00271	0.0000595	5.80E+08	0.28199	-26.6	-0.918	-14.8	1.8E+09
MR-39 BI-LH-4	0.28196	0.00005	0.00200	0.0000439	5.80E+08	0.28193	-28.9	-0.940	-16.9	1.8E+09
MR-39 BI-LH-5	0.28196	0.00006	0.00256	0.0000562	5.80E+08	0.28193	-28.8	-0.923	-17.0	1.9E+09
MR-39 BI-LH-6	0.28195	0.00009	0.00355	0.0000780	5.80E+08	0.28191	-29.0	-0.893	-17.6	1.9E+09
MR-39 BI-LH-7	0.28188	0.00008	0.00314	0.0000690	5.80E+08	0.28185	-31.5	-0.905	-20.0	2.0E+09
MR-39 BI-LH-8	0.28203	0.00010	0.00394	0.0000865	5.80E+08	0.28198	-26.3	-0.881	-15.1	1.8E+09
MR-39 BII-LH-9	0.28196	0.00006	0.00269	0.0000590	5.80E+08	0.28193	-28.8	-0.919	-17.1	1.9E+09
MR-39 BII-LH-10	0.28197	0.00007	0.00293	0.0000644	5.80E+08	0.28193	-28.5	-0.912	-16.9	1.9E+09
MR-39 média	0.28196	0.00009	0.00286	0.0000629		0.28193	-28.7	-0.9138	-17.1	1.9E+09
Plúton Quiriri										
MR-161 BII-LH-1	0.28170	0.00010	0.00162	0.00004	5.80E+08	0.28168	-38.1	-0.951	-25.9	2.2E+09
MR-161 BII-LH-2	0.28158	0.00017	0.00180	0.00004	5.80E+08	0.28156	-42.1	-0.946	-30.1	2.3E+09
MR-161 BII-LH-3	0.28173	0.00015	0.00138	0.00003	5.80E+08	0.28171	-36.9	-0.959	-24.7	2.1E+09
MR-161 BII-LH-4	0.28181	0.00044	0.00133	0.00003	5.80E+08	0.28180	-33.9	-0.960	-21.7	2.0E+09
MR-161 BII-LH-5	0.28173	0.00009	0.00144	0.00003	5.80E+08	0.28172	-36.7	-0.957	-24.5	2.1E+09
MR-161 BII-LH-6	0.28178	0.00010	0.00183	0.00004	5.80E+08	0.28176	-35.0	-0.945	-22.9	2.1E+09
MR-161 BI-LH-7	0.28177	0.00009	0.00157	0.00003	5.80E+08	0.28176	-35.3	-0.953	-23.2	2.1E+09
MR-161 BII-LH-8	0.28143	0.00010	0.00154	0.00003	5.80E+08	0.28141	-47.5	-0.954	-35.4	2.5E+09
MR-161 BI-LH-9	0.28158	0.00116	0.00176	0.00004	5.80E+08	0.28156	-42.0	-0.947	-30.0	2.3E+09
MR-161 BI-LH-10	0.28189	0.00010	0.00131	0.00003	5.80E+08	0.28187	-31.3	-0.960	-19.0	1.9E+09
MR-161 BII-LH-11	0.28165	0.00009	0.00172	0.00004	5.80E+08	0.28163	-39.8	-0.948	-27.7	2.3E+09
MR-161 BI-LH-12	0.28170	0.00008	0.00165	0.00004	5.80E+08	0.28168	-38.0	-0.950	-25.9	2.2E+09
MR-161 BI-LH-13	0.28172	0.00008	0.00136	0.00003	5.80E+08	0.28170	-37.2	-0.959	-25.0	2.1E+09
MR-161 média	0.28170	0.00021	0.00156	0.00003		0.28168	-38.0	-0.953	-25.8	2.2E+09
MR-186A CI-LH-1	0.28201	0.00015	0.00143	0.00003	5.80E+08	0.28199	-27.1	-0.957	-14.9	1.7E+09
MR-186A CI-LH-2	0.28156	0.00009	0.00164	0.00004	5.80E+08	0.28155	-42.7	-0.951	-30.6	2.4E+09
MR-186A CI-LH-3	0.28176	0.00011	0.00169	0.00004	5.80E+08	0.28174	-35.9	-0.949	-23.8	2.1E+09
MR-186A CI-LH-4	0.28146	0.00011	0.00142	0.00003	5.80E+08	0.28145	-46.3	-0.957	-34.1	2.5E+09
MR-186A CI-LH-5	0.28176	0.00011	0.00128	0.00003	5.80E+08	0.28174	-36.0	-0.961	-23.7	2.1E+09
MR-186A CII-LH-6	0.28146	0.00012	0.00141	0.00003	5.80E+08	0.28144	-46.4	-0.957	-34.2	2.5E+09
MR-186A CII-LH-7	0.28194	0.00017	0.00153	0.00003	5.80E+08	0.28193	-29.3	-0.954	-17.1	1.8E+09
MR-186A CII-LH-8	0.28163	0.00009	0.00120	0.00003	5.80E+08	0.28162	-40.3	-0.964	-28.0	2.2E+09
MR-186A CII-LH-9	0.28159	0.00018	0.00169	0.00004	5.80E+08	0.28157	-41.9	-0.949	-29.9	2.3E+09

Tabela 15: Razões isotópicas Lu-Hf (LA-MC-ICP-MS) em cristais de zircão do Complexo Morro Redondo

Amostra/Análise	$^{176}\text{Hf}/^{177}\text{Hf}$ medido	2σ	$^{176}\text{Lu}/^{177}\text{Hf}$ medido	2σ	t (Ma)	$^{176}\text{Hf}/^{177}\text{Hf}$ (i)	$\varepsilon\text{Hf}(0)$	f(Lu/Hf)	$\varepsilon\text{Hf}(t)$	$T_{\text{DM}}(1)$
MR-186A CII-LH-10	0.28176	0.00012	0.00159	0.00003	5.80E+08	0.28174	-36.0	-0.952	-23.8	2.1E+09
MR-186A CII-LH-11	0.28170	0.00007	0.00200	0.00004	5.80E+08	0.28168	-37.8	-0.940	-25.8	2.2E+09
MR-186A média	0.28169	0.00012	0.00153	0.00003		0.28168	-38.2	-0.954	-26.0	2.2E+09
Riolito Associado										
MR-254 CI-LH2	0.28189	0.00003	0.00189	0.00004	5.80E+08	0.28186	-31.4	-0.943	-19.3	1.9E+09
MR-254 CII-LH3	0.28186	0.00003	0.00196	0.00004	5.80E+08	0.28183	-32.4	-0.941	-20.4	2.0E+09
MR-254 CII-LH4	0.28185	0.00003	0.00146	0.00003	5.80E+08	0.28183	-32.8	-0.956	-20.6	2.0E+09
MR-254 CII-LH5	0.28195	0.00003	0.00231	0.00005	5.80E+08	0.28193	-29.0	-0.930	-17.1	1.9E+09
MR-254 CII-LH6	0.28198	0.00005	0.00274	0.00006	5.80E+08	0.28195	-28.1	-0.918	-16.5	1.8E+09
MR-254 CII-LH7	0.28189	0.00007	0.00237	0.00005	5.80E+08	0.28186	-31.2	-0.929	-19.3	1.9E+09
MR-254 CII-LH8	0.28186	0.00002	0.00133	0.00003	5.80E+08	0.28184	-32.3	-0.960	-20.0	1.9E+09
MR-254 CII-LH9	0.28191	0.00004	0.00211	0.00005	5.80E+08	0.28189	-30.3	-0.936	-18.4	1.9E+09
MR-254 CII-LH9_1	0.28186	0.00006	0.00281	0.00006	5.80E+08	0.28183	-32.1	-0.915	-20.5	2.0E+09
MR-254 CII-LH10	0.28182	0.00003	0.00127	0.00003	5.80E+08	0.28180	-33.7	-0.962	-21.5	2.0E+09
MR-254 CII-LH11	0.28197	0.00007	0.00252	0.00006	5.80E+08	0.28194	-28.4	-0.924	-16.7	1.8E+09
MR-254 CII-LH12	0.28184	0.00002	0.00118	0.00003	5.80E+08	0.28183	-32.9	-0.964	-20.6	1.9E+09
MR-254 média	0.28189	0.00004	0.00200	0.00004		0.28187	-31.2	-0.940	-19.2	1.9E+09

Tabela 16: Valores de $^{18}\text{O}/^{16}\text{O}$ (per mil, VSMOW) em diversos minerais dos Plúton Papanduva e Quiriri, Complexo Morro Redondo

Plúton Papanduva					Plúton Quiriri				
Amostra	Fácies	mineral	$^{18}\text{O}/^{16}\text{O}$	erro (2σ)	Amostra	Fácies	mineral	$^{18}\text{O}/^{16}\text{O}$	erro (2σ)
MR-01D	microgranítica	quartzo	7.53	0.08	MR-161	Q1	quartzo	7.66	0.06
MR-03	protomilonítica		10.15	0.12	MR-186A	Q2		8.46	0.12
MR-21	protomilonítica		9.19	0.08	MR-201B	enclave		9.08	0.06
MR-47B	cataclástica		8.42	0.06	MR-245	Q2		7.53	0.06
MR-89	maciça		7.27	0.08					
MR-39	maciça		8.39	0.1					
MR-01D	microgranítica	fels. alc.	7.39	0.04	MR-161	Q1	fels. alc.	4.47	0.14
MR-03	protomilonítica		9.09	0.14	MR-186A	Q2		7.78	0.1
MR-21	protomilonítica		6.08	0.04	MR-201B	enclave		7.60	0.04
MR-47B	cataclástica		6.21	0.08	MR-245	Q2		7.83	0.04
MR-89	maciça		2.80	0.1					
MR-39	maciça		6.08	0.12					
MR-01D	microgranítica	arfved.	3.73	0.18	MR-186A	Q2	plagiocl	7.39	0.1
MR-03	protomilonítica		5.63	0.08					
MR-03	protomilonítica		4.21	0.22					
MR-21	protomilonítica		3.62	0.12	MR-161	Q1	zircão	8.80	0.4
MR-89	maciça		2.25	0.22	MR-161	Q1		8.49	0.16
MR-39	maciça		3.34	0.06	MR-186A	Q2		4.80	0.26
MR-03	protomilonítica	egirina	6.41	0.08					
MR-03	protomilonítica		4.52	0.2					
MR-21	protomilonítica		3.03	0.18					
MR-47B	cataclástica		3.77	0.08					
MR-89	maciça		2.94	0.18					
MR-39	maciça	zircão	5.98	0.18					

ANEXO

V-17

MAPA DE PONTOS DO COMPLEXO MORRO REDONDO E ÁREAS ADJACENTES

Legenda

Fácies - Plúton Quiriri

- Q1
- Q2
- Q3
- Q4

Fácies - Plúton Papanduva

- Cataclástica
- Maciça
- Microgranito
- Protomilonito

Magmatismo bimodal contemporâneo

- Andesito
- Diabásio
- Riolito

Embasamento

- Luiz Alves

Dados estruturais

- Foliações

Elementos cartográficos

- Curvas de nível
- Drenagem

Escala Gráfica 1:100.000