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**ANÁLISES POR LA-ICPMS EM ZIRCÕES DE ROCHAS GRANÍTICAS
DA FAIXA RIBEIRA NO ESTADO DE SÃO PAULO – SE DO BRASIL:
IMPLICAÇÕES GENÉTICAS E GEOCRONOLÓGICAS**

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Metamórfica.

Orientador: Prof. Dr. Horstpeter H. G. J. Ulbrich

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RESUMO

ANDRADE, S. **Análises por LA-ICPMS em zircões de rochas graníticas da Faixa Ribeira no Estado de São Paulo – SE do Brasil: Implicações genéticas e geocronológicas.** 2016. Tese (Doutorado) - Instituto de Geociências, Universidade de São Paulo, São Paulo, 2016.

Os granitoides da Faixa Ribeira, sudeste do Estado de São Paulo, aparecem como complexas intrusões, aflorando em todos os “domínios” geológico-estruturais do embasamento paulista. Neste trabalho, foram avaliados os batólitos Cantareira, São Roque e Itaqui, os plútons Taipas e Tico-Tico, e os turmalina-granitos de Perus, no Domínio São Roque; o batólito Itu e a intrusão Terra Nova (Domínio Jundiáí); o Granito Itaquera (Domínio Embu); o granito da Ilha Anchieta e o charnockito Ubatuba (Domínio Costeiro).

Este estudo observa os padrões de evoluções petrogenéticas nos granitoides, com utilização de determinações geoquímicas e isotópicas em rochas e em zircão.

A espectrometria de massa (por quadrupolo) associada à ablação a laser (LA-Q-ICPMS) foi aplicada para determinar elementos traço em zircão. Dados analíticos de materiais de referência (zircão 91500 e zircão GJ-1) são apresentados no capítulo sobre metodologias.

Os dados lito-geoquímicos indicam que as amostras pertencem a linhagens metaluminosas a peraluminosas com elevados teores de K. Granitos metaluminosos (Cantareira, Itaqui, etc.) mostram elevados teores de Sr e da razão Sr/Y, sem anomalia de Eu, em magmas provavelmente formados em profundidade, com granada estável. Os demais granitos mostram-se compatíveis com origem a pressões menores, com plagioclásio estável (anomalia negativa de Eu, baixos teores de Sr).

Os zircões, em geral, mostram teores elevados de ETR, Th e U. Os diagramas normalizados de ETR mostram anomalias positivas de Ce, geradas em ambiente oxidante. Os zircões das amostras Tico-Tico, Itu, Terra Nova, Ilha Anchieta, Itaquera, Perus e charnockito Ubatuba apresentam anomalias negativas de Eu, provavelmente determinada pela co-cristalização com plagioclásio.

Os elevados teores de ETR e Y nos zircões indicam a atuação de reações acopladas tipo xenotima, com substituição de Si^{4+} por P^{5+} e de Zr^{4+} por ETR^{3+} , Y^{3+} .

O geotermômetro Ti-em-zircão ($T_{zir.}$) rendeu, em geral, temperaturas de cristalização equivalentes às temperaturas de saturação de zircão e apatitas em magmas. Zircões com núcleos reabsorvidos e com reflexão escura em CL apresentaram T_{zir} não realistas, acima de 1000°C , devidas a incorporação exagerada de Ti junto com ETR e P, por influencia de fluidos hidrotermais, que transportam também outros elementos HFS (Nb, Ta, Mo).

Os resultados de idades U-Pb em zircão destes granitóides levam a valores entre 580 a 603 Ma, 30 Ma mais jovens que os da literatura.

As razões Lu-Hf mostram similaridade entre os protólitos dos granitos São Roque e Itaquera, com uma possível fonte Paleoproterozóica (~ 2.9 Ga) e com ϵHf de -22.8, de elevada residência crustal; as idades TDM (Sm-Nd) estão entre 2.2 e 2.5 Ga, possivelmente representando uma fonte crustal associada a Paleoplaca São Francisco. Para os demais granitoides (Domínios São Roque e Jundiá) é necessária uma fonte mais radiogênica para os valores de ϵHf (-18 a -11) e ϵNd (-12 a -9). As idades TDM, e as mais antigas U-Pb obtidas em alguns núcleos herdados de zircão, indicam fonte constituída por crosta continental juvenil acrescida durante evento vulcânico (por rifteamento) em 1.75 Ga, dentro da placa tectônica, devido a abertura continental, ou mesmo durante eventos ocorridos cerca de 2.1 Ga dentro de Cráton São Francisco.

Palavras chaves: LA-ICPMS, granitos Brasileiros, elementos traço, zircões, fluidos hidrotermais, geocronologia.

ABSTRACT

ANDRADE, S. **Analytical determinations by LA-ICPMS in zircons from granitic rocks of the Ribeira Belt in the state of São Paulo – SE of Brazil: Genetic and geochronological implications.** 2016. Tese (Doutorado) - Instituto de Geociências, Universidade de São Paulo, São Paulo, 2016.

The granitoids of the Ribeira Belt, southeastern São Paulo state, southeastern Brazil, are found as complex intrusions spread out uniformly in all structural-geologic “domains” of the São Paulo basement area. In our work, samples were studied from the Cantareira, São Roque and Itaquí batholiths, the Taipas and Tico-Tico plutons and the Perus tourmaline granites (São Roque Domain), the Itu batholith and the Terra Nova intrusion (Jundiaí Domain), the Itaquera granite (Embu Domain), the Ilha Anchieta granite and the Ubatuba charnockite (Costal Domain).

This study aims to unravel the pattern of petrogenetic evolution in the granitoids, with the help of geochemical determinations in rocks and zircon crystals.

Quadrupole mass spectrometry with laser ablation (LA-Q-ICPMS) was applied to determine trace elements contained in zircons. Analytical data for reference materials (zircons 911500 and GJ-1) are presented in the chapter on Methodology.

The lithogeochemical data show that the granites represent meta-aluminous to peraluminous lineages, with significant potash contents. Meta-aluminous samples (Cantareira, Itaquí, etc.) are high in Sr, also with high Sr/Y ratios and no Eu anomalies, representing magmas probably formed at considerable depth, implying garnet stability. The other granites were formed from magmas at lower pressures (stable plagioclase; negative Eu anomaly; low Sr contents).

Zircons from these granites contain high REE, U and Th abundances. Normalized REE diagrams present positive Ce anomalies, generated in oxidizing environments. Zircons from Tico-Tico, Itu, Terra Nova, Ilha Anchieta, Itaquera, Perus and the Ubatuba charnockite are characterized by negative Eu anomalies, probably controlled by co-crystallization with plagioclase.

The high REE and Y contents in zircons are explained by coupled xenotime-type reactions, with substitution of Si^{4+} by P^{5+} and Zr^{4+} by REE^{3+} , Y^{3+} .

The Ti-in-zircon geothermometer (T_{zir}) yields, in general, temperatures comparable to the ones obtained with the saturation temperatures of zircons and

apatites in magmas. Zircons showing reabsorbed cores and dark reflection areas under CL yield unrealistic temperatures above 1000°C, explained by anomalous uptake of Ti, together with high REE and P contents, on account of hydrothermal fluid activity, also responsible for transporting other HFSE (Ta, Nb, Mo).

Dating results with the U-Pb technique in zircons show values between 580 and 603 Ma, 30 Ma younger than results previously published.

Lu-Hf ratios suggest similarities for the protoliths of the São Roque and Itaquera granites, with a possible Paleoproterozoic source (~2.9 Ga) and with ϵ_{Hf} of -22.8, indicating protracted crustal residence time. TDM ages (Sm-Nd) lie between 2.2 and 12.5 Ga, possibly representing a crustal source associated with the São Francisco paleoplate. For the other granitoids (São Roque and Jundiá domains), a more radiogenic source has to be considered, given the ϵ_{Hf} (-18 to -11) and ϵ_{Nd} (-12 to -9) values. TDM ages, and the older ages obtained with U-Pb on cores of some zircons, point to a source constituted by juvenile continental crust affected by a volcanic event (rifting) at 1.75 Ga, within the tectonic plate, forced by continental opening, or even during events that occurred close to 2.1 Ga within the São Francisco craton.

Key words: LA-ICPMS, Brasileiro granites, trace elements, zircons, hydrothermal fluids, geochronology.

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PARTE I - INTRODUÇÃO

I.1. APRESENTAÇÃO E ESTRUTURAÇÃO DA TESE

Esta Tese apresenta estudo metodológico e geoquímico de algumas rochas granitóides selecionadas no Estado de São Paulo. Essas rochas aparecem como ocorrências complexas tanto do ponto de vista petrográfico quanto estrutural, pois ocorrem em intrusões múltiplas com dimensões de pequenas a moderadas (diques, bossas, plútons limitados) até batolíticas; em conjunto, atingindo até 30% da superfície exposta do embasamento (Janasi; Ulbrich, 1991, 1992). Aparentemente, não existe localização preferencial dessas intrusões graníticas, pois elas estão colocadas indistintamente em todos os “domínios” ou “blocos” geológico-estruturais em que pode ser dividido o embasamento do Estado de São Paulo, invadidos por igual por granitóides, independentemente do tipo de rocha encaixante e do seu grau metamórfico.

Neste trabalho se utilizaram as determinações multielementares em rochas e em minerais (zircão) de granitóides presentes em várias das unidades geológicas do Complexo Ribeira a fim de se verificar identidades ou discrepâncias em padrões de elementos traço. Este estudo teve como propósito observar padrões de evoluções petrogenéticas paralelas ou diferenciadas nas unidades cálcio-alcálicas e em seus derivados evoluídos. Determinações, quando possível, das razões isotópicas nos sistemas U-Th-Pb, e Lu-Hf foram também obtidas como uma linha adicional de evidências para essas interpretações petrogenéticas.

A Tese está organizada em cinco partes principais. A Parte I apresenta uma breve introdução à temática abordada, com apresentação da área de estudo e dos principais objetivos alcançados. Na Parte II são descritos os materiais e métodos empregados para a obtenção dos objetivos pretendidos. A Parte III reúne algumas considerações sobre os resultados obtidos quanto à assinatura isotópica de Rb-Sr, Sm-Nd em rochas e U-Pb e Lu-Hf em zircão para os granitoides dos Domínios Embu, Jundiá e Costeiro, com algumas interpretações petrogenéticas e tectônicas

mais relevantes. A Parte IV traz, na forma de anexos, três textos, um deles em vias de submissão, e dois correspondendo a trabalhos já publicados em periódicos especializados. Por fim, na Parte V são reunidos, na forma de tabelas, os resultados analíticos obtidos, bem como figuras que não puderam ser incluídas no texto, mas que são importantes para caracterizar o trabalho desenvolvido.

I.2. TEMÁTICA

A técnica de *laser ablation* unida à espectrometria de massa com plasma induzido acoplado (LA-ICPMS) tem provado ser uma poderosa ferramenta para determinações pontuais de elementos traço e relações isotópicas, com importantes aplicações nas ciências geológicas. A amostragem por *laser ablation* requer muito pouco material, tipicamente da ordem de nanogramas ou microgramas por pulso. Associada a esta característica aparece também à elevada resolução espacial, com furos (*spots*) da ordem de 10 a 300 μm e resolução de profundidade em torno de 60 nm por pulso. Essas características associadas às do ICP-MS, que permite análises multielementares rápidas, com sensibilidade da ordem de ng.g^{-1} (ppb), possibilitam a caracterização química com determinações de 35 elementos (ou mais) em minerais homogêneos e/ou zonados, ou de pequenas gotas de materiais fundidos ocluídos em rochas (*melts*), inclusões fluídas, etc., em tempos que variam de 1 a 2 minutos mesmo em determinações de razões isotópicas.

A importância do zircão como mineral acessório se deve a combinação de vários fatores, tais como a tendência a incorporar elementos traço (inclusive radionuclídeos), sua resistência aos processos físicos de atrito e aos ataques químicos, e também sua marcante resistência ao reequilíbrio difusivo em elevadas temperaturas e pressões, observadas principalmente durante processos de litificação, metamorfismo e fusão parcial (Watson, 1996; Watson; Cherniak, 1997). Embora a abundância de zircão seja baixa nas rochas, ele está amplamente distribuído em rochas crustais e xenólitos do manto (Speer, 1980). Sua presença afeta fortemente o comportamento de muitos elementos traço durante a cristalização de magmas (Belousova et al., 2002) e, por esse motivo, a compreensão de sua

composição química é fator de grande importância para o modelamento petrológico (Nagasawa, 1970; Watson, 1979; Murali et al., 1983).

O magmatismo granítico é fundamental para o estudo da evolução da crosta continental. O caráter das rochas crustais de suítes intrusivas graníticas é tipicamente obscurecido pela possível mistura e homogeneização de magmas crustais com fundidos derivados do manto, que representam a sua rocha fonte. Quantificar a contribuição dos vários elementos químicos mobilizados para gerar uma crosta continental, em boa parte relacionada com a geração de rochas granitoides, somente é possível através de uma melhor caracterização do comportamento desses elementos e da sua incorporação durante processo de fusão parcial (direta ou indiretamente de origem mantélica) e sua posterior fixação, durante a cristalização dos magmas, em redes cristalinas não só dos minerais formadores de rochas como dos acessórios. Este aspecto realça a importância do estudo dos minerais como zircão, e de sua evolução, sendo eles importantes hospedeiros de vários elementos traço (U, Th, ETR, etc.).

O conhecimento sobre as rochas Pré-Cambrianas do Estado de São Paulo tem apresentado avanços consideráveis com a aplicação da análise estrutural nos terrenos metamórficos e de novas técnicas analíticas para a geração e interpretação de dados químicos de granitoides e a integração com dados estruturais e de associações litoestruturais específicas. Várias tentativas de compilação e classificação mais abrangente desses granitoides, em especial os localizados no S-SE brasileiro, aparecem na literatura, tipicamente separando essas ocorrências granitoides em tipos pré-, sin-, tardi- e pós-tectônicos (e.g. Hasui et al., 1978a; 1978b; Carneiro, 1983; Dantas, 1990; Janasi; Ulbrich, 1991, 1992). No nosso estudo, foram selecionados exemplos característicos desses granitoides, alguns deles muito citados na literatura, geralmente estudados pelo menos em parte com grande detalhe (regional, geológico e petrográfico). Um aspecto que deve ser lembrado é que os granitoides aqui selecionados para estudos são aqueles que podem ser coletados como fragmentos de rocha fresca de vários quilogramas, portanto, de dimensões adequadas para realizar os estudos pretendidos (em particular, permitir a separação de algumas centenas de grãos de zircão e outros minerais acessórios, um número imprescindível para coletar populações representativas desses minerais). O acesso a pedreiras e amplos cortes de estrada,

portanto, torna-se naturalmente um critério prioritário para a seleção dessas rochas como objeto de estudo, visto nem sempre ser fácil à obtenção de amostras frescas em quantidades adequadas. No caso de granitos infelizmente é muito comum que sejam representados no terreno apenas por afloramentos esporádicos na forma de matacões, e mais raramente como lajedos. A maioria de nossas amostras é representativa de suítes cálcio-alcálinas, algumas delas mostrando dimensões batolíticas (Cantareira, Itaqui, São Roque, Itu), que representam as linhagens mais abundantes citadas entre os granitoides em São Paulo, enquanto outras são notáveis exemplos de evolução magmática mais específica ou até extrema, tais como os coletivamente denominados de “turmalina granitos” de Perus, com elevadas concentrações de elementos traços (entre eles Li e B) e granitoides a duas micas, como Tico-Tico ou Itaquera, representantes das chamadas suítes “S” de evolução magmática.

Neste trabalho o uso de diferentes técnicas analíticas como ferramenta possibilitou a obtenção de informações geoquímicas e isotópicas, tanto das rochas granitoides quanto do mineral acessório zircão nelas presentes, permitindo assim analisar as características peculiares desses exemplares. O paralelo geoquímico traçado entre os diversos granitoides aflorantes nessa região do Estado de São Paulo permite contribuir para o estudo da gênese e evolução desses corpos graníticos representativos.

1.3. GEOLOGIA REGIONAL DO ESTADO DE SÃO PAULO

O embasamento na parte sul do Estado de São Paulo faz parte da Província Mantiqueira, com evolução atribuída por Almeida e Hasui (1984) ao Proterozóico e Arqueano. A Província Mantiqueira, representante do Escudo Atlântico, aparece como uma faixa ao longo da região costeira entre o sul da Bahia até o Rio Grande do Sul, com cerca de 3000 km de comprimento e 200 km de largura na parte sul, e de 600 km na parte norte. Para oeste faz limite com o Cráton do São Francisco, com a extremidade sul do Cinturão Brasília do Sistema Orogênico Tocantins e com a cobertura da Bacia do Paraná. Para leste mostra contato com a Província da

Margem Continental Leste. O Sistema Mantiqueira é formado essencialmente por rochas Pré-Silurianas (>450 Ma), com registros dos processos de divergência ocorridos no Ciclo Brasileiro, durante o Pré-Cambriano, que acarretaram a fragmentação do Supercontinente Rodínia e também da deriva de continentes, com abertura de oceanos, seguidos de outros períodos de convergência, que resultaram na reaglutinação de fragmentos continentais para a formação do megacontinente Gondwana (no Triássico se junta este continente a outras massas continentais para gerar o Continente Pangeia). Uma etapa final que encerrou o Ciclo Brasileiro foi a do colapso gravitacional e exumação de orógenos, marcando a passagem de condições de forte atividade compressiva, com aglutinação de continentes e fechamento de oceanos, para as de estabilização intraplaca. Essa etapa derradeira se estendeu até o Ordoviciano Superior, por volta de 450 Ma, concomitantemente com o início da subsidência da Bacia do Paraná.

O Sistema Mantiqueira foi compartimentado em três setores, referidos por Almeida e Hasui (1984) como setentrional, central e meridional. Essa divisão se manteve através dos tempos, com alteração dos limites em função do avanço dos conhecimentos geológicos e geocronológicos. Com estes novos conhecimentos, os compartimentos passaram a ser considerados como correspondentes a três cinturões orogênicos: Araçuaí correspondendo à parte setentrional, Ribeira à central e Tijuca à parte meridional (Figura 1.1; ver também Hasui et al., 2012).

Figura 1.1. Sistema orogênico Cantareira indicando sua compartimentação nos três cinturões Araçuaí, Ribeira e Tijuca, segundo Almeida e Hasui 1984. A cobertura fanerozóica está indicada em amarelo (Hasui et al, 2012).

O Neoproterozóico Cinturão Ribeira no sudeste do Brasil é desenvolvido ao longo da borda SE do Cráton São Francisco durante a convergência com outra placa localizada a leste (Brito Neves et al., 1999, Heilbron; Machado, 2003). Modelos tectônicos para evolução da parte central do cinturão Ribeira (Estado do Rio de Janeiro) propõe subducção da paleoplaça do São Francisco, formando o Arco Magmático Rio Negro no Terreno Oriental que foi eventualmente acrescido ao continente São Francisco através de uma colisão frontal, que teria durado de 590 a 550 Ma (Heilbron; Machado, 2003). Este evento foi seguido por acreção aos terrenos Cabo Frio num novo evento colisional, ou de ancoramento, a 535-510 Ma (Schmitt et al., 2004) e, finalmente, pelo colapso orogênico em 510-480Ma.

O cinturão Ribeira, segundo Hasui et al. (2012), se limita com o Cinturão Araçuaí na região da divisa Minas Gerais - Rio de Janeiro - São Paulo. Ele se estende para sudoeste até o Paraná e leste de Santa Catarina. Para oeste é coberto pela Bacia do Paraná e a leste faz limite com a Província da Margem Continental

Leste. No centro-sul de Minas Gerais relaciona-se com a porção sul do Cinturão Brasília, e sua extremidade sul com o Cinturão Tijucas (Figura I.1).

As áreas do embasamento Pré-Cambriano no Estado de São Paulo, em boa parte coincidente com o Complexo Ribeira, foram divididas por Janasi e Ulbrich (1991, 1992) em oito domínios chamados, neste contexto, de São Roque, Açungui, Embu, Ubatuba, Iguape, Guaxupé, Jundiaí e Amparo (Tabela I.1). Estes blocos estruturais alongados são limitados por importantes falhas transcorrentes, curvadas e interconectadas, as quais podem atingir até centenas de quilômetros de comprimento (Figura I.2).

Os metassedimentos, hoje rochas metamórficas de baixo grau representativas do ciclo Brasileiro, parecem estar restritos a parte do Domínio Açungui (Janasi e Ulbrich, 1991). As rochas metamórficas de baixo e médio grau (provavelmente supracrustais, xistos com cianita $\pm$ estaurolita) do Mesoproterozóico aparecem nos Grupos São Roque, Açungui, Amparo e parte dos domínios Embu e Iguape (Bistrichi et al., 1981). As áreas melhor estudadas do Grupo São Roque e Açungui mostram unidades vulcano-sedimentares como rochas supracrustais. As áreas que foram mais fortemente afetadas pelo metamorfismo de alto grau do ciclo Brasileiro foram as dos domínios Ubatuba e Guaxupé, que mostram predominantemente ortognaisses, e os de Jundiaí e em parte de Embu, que apresentam rochas supracrustais contendo granadas, sillimanita, K-feldspato e muscovita. Os migmatitos, ortognaisses e granulitos, possivelmente do Arqueano-Proterozóico, predominam no Domínio Iguape, rochas que foram reconhecidas como embasamento para as sequências supracrustais dos domínios de Amparo e Embu (Tassinari, 1988). Segundo Janasi e Ulbrich (1991, 1992), estas rochas também podem estar presentes nos domínios Guaxupé, Jundiaí e Ubatuba, mas foram fortemente retrabalhados no ciclo Brasileiro.

Tabela I.1. Os domínios geológicos no embasamento paulista (Janasi e Ulbrich, 1991, 1992)

Domínio	Características das rochas metamórficas predominantes
<i>Iguape</i>	Embasamento de rochas arqueanas e paleoproterozóicas (migmatitos, ortognaisses e granulitos do Complexo Costeiro) e faixa de xistos supracrustais mesoproterozóicos de grau baixo a médio (Complexo Paraibuna).
<i>Ubatuba</i>	Ortognaisses (Paleoproterozóico?; Arqueanos?) de alto grau (Complexo Costeiro).
<i>Embu</i>	Complexo Embu (para NE: granada-sillimanita xistos e paragnaisses de alto grau) e Complexo Pilar (para SW: xistos e filitos Mesoproterozoicos de grau baixo a médio).
<i>Açungui</i>	De NW para SE: faixa setentrional, sequência meta-vulcano-sedimentar de baixo grau (Grupo Itaiacoca); faixa central e meridional, meta-supracrustais de baixo grau (Grupos Açungui e Lajeado).
<i>São Roque</i>	Grupo São Roque, superior, metassedimentos brasileiros (ou pré-brasileiros?), de baixo grau; Grupo Serra de Itaberaba (Meso a Paleoproterozóicos), inferior, com rochas metabásicas, mármore, metassedimentos, em grau baixo a médio.
<i>Jundiaí</i>	Complexo Piracaia: predominam rochas supracrustais de alto grau, parcialmente migmatizadas (biotita gnaisses e xistos, em parte com granada e sillimanita; quartzitos).
<i>Amparo</i>	Grupo Andrelândia e Itapira: rochas supracrustais Mesoproterozóicas de grau baixo a médio.
<i>Guaxupé</i>	Rochas supracrustais de alto grau do Complexo Pinhal.

As unidades metamórficas predominantes nos domínios identificados por Janasi e Ulbrich (1991, 1992) mostram um variado número de granitoides. As mais de 200 ocorrências citadas na literatura podem ser agrupadas em tipos diferentes, em função de suas características geológicas, petrográfico-mineralógicas e estruturais-texturais, e ainda as suas idades (Janasi; Ulbrich, 1991 e 1992). São identificadas as seguintes associações: uma antiga de ortognaisses de embasamento, tonalíticos a graníticos de provável idade Paleoproterozóica a Pré-Paleoproterozóica (estabilização de áreas cratônicas Arqueanas, por volta de 2500 Ma); uma suíte mangerítica a charnoquítica deformada, de idade incerta, talvez Mesoproterozóica, representando uma associação anorogênica; o conjunto dos

grandes batólitos de biotita e hornblenda-biotita granitoides (e augen-gnaisses) pré-orogênicos; a associação de granitoides migmatíticos; os muscovita-biotita granitoides peraluminosos sin- e tardi-orogênicos; os biotita-granitos a granodioritos cálcio-alcálinos sin- e tardi-orogênicos; e, finalmente, as ocorrências pós-orogênicas. Um esquema simplificado de distribuição destas associações é reproduzido na Figura I.2.

Figura I.2. Algumas das principais ocorrências de granitoides no Estado de São Paulo, SE do Brasil (Janasi e Ulbrich, 1991, 1992). A1: Natividade da Serra, A2: Paraibuna, A3: Ubatuba, B1: Alto Turvo, B2: Guaraú, B3: Mandira, B4: Ilha do Cardoso, C1: Serra do Quebra-Cangalha, C2: Lagoinha, C3: Butantã-Santa Isabel, C4: Ibiuna, C5: Jurupará, C6: Três Lagos, Itapissera, D1: Cantareira, D2: Itaqui, D3: São Roque, D4: São Francisco, D5: Sorocaba, D6: Tico-Tico, E1: Três Córregos, E2: Capão Bonito, E3: Itaoca, E4: Sguario, E5: Campina do Veado, F1: Socorro, F2: Camanducaia, F3: Campos de Jordão, F4: Morungaba, F5: Piracaia, F6: Nazaré Paulista, F7: Itu, H1: Pinhal-Ipiúna, H2: São José do Rio Pardo, H3: Pinhal (divisa com outros granitoides pouco caracterizados), TB: Bacia de Taubaté, F: Falhas.

A seguir é apresentado um resumo dos principais dados geológicos que foram compilados da literatura sobre os diversos granitoides focalizados neste trabalho, presentes nos Domínios Embu, São Roque, Jundiaí e Costeiro (região de Ubatuba).

I.3.1. Domínio São Roque

O Grupo São Roque caracteriza-se por apresentar protólitos depositados em ambiente marinho (Moraes Rego, 1933), com atividade vulcânica submarina (Carneiro et al., 1984). Limita-se ao norte pela falha de Jundiuvira, a oeste por sedimentos da bacia do Paraná, a sul pela falha de Taxaquara e a leste pela intersecção das falhas de Monteiro Lobato e Jundiuvira (Figura I.2). Hasui et al. (1976) fazem a primeira subdivisão do Grupo São Roque, reconhecendo na região de Pirapora uma formação inferior – Boturuna - constituída de metapelitos, metaconglomerados e metacalcários e uma formação de topo - Piragibu - constituída por quartzitos, metassiltitos e filitos.

Uma sequência vulcano-sedimentar presente na região da Serra do Itaberaba foi caracterizada como a base do Grupo São Roque (Coutinho et al., 1982), sendo composta por vulcânicas e sub-vulcânicas básicas e seus tufos, bem como camadas argilosas, margas e intercalações de sedimentos químicos silicosos. Acima desta sequência foi descrito um pacote com menor metamorfismo, representado na base por “metarcóseos rítmicos” sucedido por filitos com intercalações quartzíticas (Campos Neto; Basei, 1983). A sequência basal foi posteriormente distinguida como Grupo Serra do Itaberaba por Juliani et al. (1986), que a subdividiram em três formações, a Formação Morro da Pedra Preta (basal) composta por rochas metavulcanoclásticas, calciossilicáticas, e formações ferríferas, sobreposta pela Formação Nhanguçu, com sedimentos clasto-químicos, e a Formação Pirucaia, formada por rochas essencialmente quartzíticas, que corresponderia às fácies marginais da bacia, que seria cronocorrelata às outras duas. Esta sequência foi separada do Grupo São Roque principalmente por tratar-se de rochas que registram, durante o desenvolvimento da foliação S1, um grau metamórfico predominantemente da fácies anfibolito médio, em contraposição ao Grupo São Roque (fácies xistos verdes). O contato erosivo entre os dois grupos seria atestado pela presença de clastos de fragmentos vulcânicos relacionados ao Grupo Serra do Itaberaba nos metaconglomerados da base do Grupo São Roque (Juliani, 1993; Martin, 2000).

Juliani et al. (2000) apresentaram idade U-Pb em zircão de 1395 ± 10 Ma para um meta-andesito da Formação Morro da Pedra Preta, posicionando a deposição do Grupo Serra do Itaberaba no Mesoproterozóico. A zona de falhamento transcorrente de Jundiuvira foi caracterizada como uma descontinuidade limítrofe entre blocos, separando o “Bloco São Roque” do “Bloco Jundiáí”, situado a norte (Hasui et al., 1969). As rochas da região da Serra do Japi foram incluídas por Wernick et al (1976) no Grupo Amparo, e divididas em membros pelíticos (Formações Ermida) e psamo-pelíticos (Formação Japi), sem continuidade com as rochas do Grupo São Roque, o que também foi observado por Hasui et al. (1978a). No entanto, Moraes (1944) e Campos Neto (2000) admitem que os metassedimentos da Serra do Japi constituam continuidade do Grupo São Roque a norte deste limite. O magmatismo granítico é intenso no Domínio Apiaí-São Roque, caracterizado por Campos Neto (2000) como um arco magmático desenvolvido na margem do Cráton Paranapanema. É dominado por granitos cálcio-alcálicos potássicos Neoproterozóicos, que constituem a massa principal de três extensos batólitos alongados na direção NE-SW (Cunhaporanga, Três Córregos e Agudos Grandes) aflorantes nos estados de Paraná e São Paulo. Inúmeros corpos isolados de menor volume, incluindo as principais intrusões no Domínio São Roque, devem constituir satélites dessas grandes massas graníticas, tendo em vista as semelhanças composicionais e de idade (Janasi; Ulbrich, 1991, 1992).

1.3.1.1. Domínio São Roque: rochas granitoides

No detalhado mapa de compilação efetuado por Azevedo (1997) em área vizinha à cidade de São Paulo (zona de Perus), que engloba as folhas geológicas de Guarulhos e Santana de Parnaíba, aparecem identificadas as rochas encaixantes metamórficas do Grupo São Roque e vários granitoides intrusivos nessa região. Este mapa foi baseado nos mapas preparados por diversos autores (Carneiro, 1983; Bergmann, 1988; Dantas, 1990; Ferreira, 1997) e permite estabelecer as bases para interpretações geológicas mais abrangentes.

Nos metassedimentos ocorrem vários corpos granitoides intrusivos considerados de colocação pré-, sin- a tardi- e pós-tectônica segundo Dantas (1990). Os mais antigos, pré-tectônicos, localizam-se na parte setentrional e caracterizam-se estes maciços por apresentarem formas alongadas, distribuídos em faixas próximas às principais zonas de cisalhamento; estão normalmente intensamente deformados por efeito das sucessivas etapas de deformação. Os granitoides considerados sin- e tardi-tectônicos são de idade brasileira e aparecem distribuídos em parte como maciços maiores; são cortados por inúmeras falhas, com alguns sinais de deformação localizada. Tanto os maciços pré-tectônicos como os de filiação brasileira apresentam biotita granitos, em boa parte porfiríticos, como litotipos predominantes; alguns maciços (ou fácies mais evoluídas de maciços maiores) são constituídos por granitos a duas micas, tipicamente também com alguma granada, e por turmalina granitos.

Os maciços considerados pré-tectônicos são os seguintes: Barroca Funda, Francisco Morato, Vargem Grande, Mato Dentro, Pedra Vermelha e Vila dos Remédios. O posicionamento estratigráfico desses granitoides é incerto, uma vez que existem poucos dados sobre as suas idades e as possíveis relações genéticas, tanto entre si como frente aos granitoides brasileiros. A falta de dados não exclui a possibilidade de que alguns representem rochas do embasamento. Alternativamente eles podem ser em parte equivalentes deformados (sintectônicos?) de alguns dos maciços brasileiros, devido à semelhança mineralógica entre os granitoides de Perus e Tico-Tico com alguns granitoides “pré-tectônicos” a duas micas e com turmalina, tais como os dos maciços: Francisco Morato, Pedra Vermelha e do Mato Dentro, ou a presença de enclaves no biotita-granito Barroca Funda, sugerindo tratar-se de ocorrências evoluídas a partir de magmas iniciais de filiação cálcio-alcalina (portanto também brasileiros?).

I.3.1.1. a. Granitoides Brasileiros

Os granitoides considerados brasileiros foram anteriormente classificados em função de suas feições características e subdivididos em sin-, tardi- e pós-tectônicos

(e.g. Hasui et al, 1978a; Carneiro, 1983; Dantas, 1990, ver também bibliografia em Janasi; Ulbrich, 1992). São encontrados desde maciços de dimensões menores ou médias, até aqueles que constituem as maiores unidades granitoides presentes na região. Entre os primeiros, são citados os coletivamente denominados de “turmalina granitos” de Perus, claramente muito diferenciados. As ocorrências de dimensões intermediárias são o Maciço Tico-Tico (a duas micas e granada), Mairiporã (com biotita como máfico principal ou único), Ponunduva (fortemente cataclasado e alterado) e Taipas (com biotita e anfibólio). Os de maiores dimensões são os batólitos Itaqui e Cantareira, que em parte se expandem também para as folhas vizinhas, mais para o Sul (Domínio Embu).

De acordo com Dantas (1990) as feições mineralógico-petrográficas e geoquímicas mostram que estes granitoides pertencem a linhagens muito diferentes. Encontram-se granitos com características claramente ou marginalmente cálcio-alcalinas (e.g., maciços Taipas e Cantareira, e as fácies mais importantes do maciço Itaqui) até os de derivação crustal (e.g. maciço Tico-Tico e as fácies mais evoluídas do Itaqui). Notáveis, mas de ocorrências muito restritas, são as bossas e os diques altamente diferenciados que formam o conjunto de turmalina-granitos de Perus e alguns dos litotipos de menor expressão do Itaqui, todos com turmalina e/ou granada como minerais máficos, e cujos elevados teores de Li, U e outros elementos permitem a cristalização de micas com Li e minerais tardios de U.

As datações geocronológicas U-Pb, principalmente em zircão, mostram idades coincidentes para muitas manifestações (Itaqui 624 ± 11 Ma para a fácies Barueri; Tico-Tico 625 ± 18 Ma; Cantareira 630 ± 8 Ma (cf. Tassinari et al., 1985; Van Schmus et al., 1986; Tassinari, 1988). Assim, a proximidade geográfica entre estes maciços graníticos, todos situados no Domínio São Roque e com relações claramente intrusivas, mostra que eles não deveriam ser classificados como maciços sin-, tardi- ou pós-tectônico, tão somente em função da forma e alongação, presença de estruturas internas, texturas porfiríticas ou mais equigranulares, e caráter mais ou menos “cálcio-alcalino”.

As principais feições mostradas por estes granitoides são descritas a seguir, principalmente em função dos dados apresentados na literatura (compilação em Azevedo, 1997).

O Maciço Itaquí, mapeado em detalhe por Ferreira (1991), é constituído por variado conjunto de intrusões sucessivas, predominantemente com fácies cálcio-alcalinas. Mostra forma triangular, alongado no sentido WNW-ESE, com superfície exposta da ordem de 120 km², e que no seu limite meridional aparece em contato com a zona de cisalhamento Taxaquara. Nele foram identificadas dez fácies diferentes, que ascenderam durante quatro pulsos magmáticos relacionados a dois episódios ou “ciclos” intrusivos diferentes.

Os primeiros pulsos ou acreções são de rochas granitoides com textura porfirítica (o *granodiorito Barueri* e o *monzogranito Pedreira Cantareira*, com biotita e hornblenda). Culmina a fase com a intrusão de *diques do biotita-monzogranito Torre* (equigranular, granulação fina), os diques de *monzogranito porfiróide* a equigranular (com biotita a hornblenda), e os *diques de quartzo monzonito Cruz Preta* (porfirítico com biotita). Os *biotita-monzogranitos Aldeia da Serra e Mutinga*, com textura inequigranular a porfirítica, representariam a terceira fase de acreção. A última fase estaria representada pela invasão de corpos menores, os *diques monzograníticos Suru*, equigranulares e com biotita, e os aplitos com turmalina e sericita. Considera Ferreira (1991) que a intrusão principal ocorreu entre a segunda e a terceira fase de deformação regional, sendo ainda duvidoso o posicionamento dos aplitos com turmalina (Ferreira, 1991; Wernick et al., 1993, 1995).

Ao norte do batólito de Itaquí encontra-se o **Granito Itaim**, descrito por Coutinho (1972) e Carneiro (1983), denominado também Fazenda ou **Granja Itahye** (Janasi; Ulbrich, 1992). Esse maciço de forma alongada, com eixo maior na direção N-S (2 km), sendo mais estreito na porção central, é um granito tipo Pirituba (biotita-granito porfirítico). Apresenta cristais centimétricos de K-feldspato róseo ou branco em matriz cinzenta, média a grosseira, pouco orientada (Janasi; Ulbrich, 1992).

O **Maciço ou “Complexo” Cantareira**, uma das maiores manifestações granitóides do Estado de São Paulo, mostra complexa estrutura interna. Tem forma alongada segundo direção NE-SW, com superfície aflorante da ordem de 320 km². Os contatos são tectônicos e estão limitados por falhas vizinhas a de Caieiras (parte setentrional) e pela zona de cisalhamento de Mandaqui (região ocidental).

Azevedo (1997) descreve o granito Cantareira como o maior corpo da região. Dantas (1990) reconheceu nove fácies ou “tipos” distintos nesse maciço. A fácies ou *tipo Pirituba* (fácies porfiróide creme), predominante no centro e SE do maciço, é de

biotita granodioritos a monzogranitos porfiróides, com rara hornblenda, mais rica em enclaves; mostra fenocristais bege de microclínio, sem orientação. O *tipo Canivete* (fácies porfiróide cinza azulada) é composto principalmente por monzogranitos porfiróides, com megacristais não orientados de microclínio cinza e abundantes enclaves microgranulares; predomina na parte SW do maciço. O *tipo Itaguaçu* (fácies porfiróide rósea) é caracterizado por bolsões de monzogranitos e granodioritos porfiróides; são comuns os enclaves micáceos e os sulfetos em fraturas. O *tipo Mandaqui* (fácies ortognáissica) mostra composição granodiorítica a monzogranítica porfiróide, com megacristais arredondados localizados em matriz deformada milonítica a blastomilonítica, aparecendo principalmente nas margens do corpo e em zonas de falha. O *tipo Tremembé* (fácies equigranular cinza) aparece como bolsões irregulares e diques métricos, dispersos por todo o maciço; são monzogranitos de cor cinza claro, equigranulares e com enclaves, e posteriores ao Pirituba. O *tipo Petrópolis* (fácies pegmatóide) que ocorre como bolsões irregulares, constitui-se de granodioritos a monzogranitos porfiróides ricos em megacristais; são encontrados enclaves microgranulares e micáceos. O *tipo Hortolândia* (fácies inequigranular cinza) é de monzogranitos a granodioritos inequigranulares de cor cinza, orientados e com enclaves, que aparecem como corpos alongados na margem NE do maciço mostrando gradações para os tipos porfiróides. A *fácies Santa Inês* (migmatítica ou bandada) é de granodioritos porfiróides, ricos em biotita e com clara estrutura de fluxo (aspecto “bandado” da rocha), encontrados como fácies da borda norte. Finalmente, o *tipo Jaraguá* (fácies inequigranular leucocrática) é formado por bolsões irregulares e diques métricos de leuco-quartzo monzonitos esbranquiçados, mostrando em partes forte alteração hidrotermal. Estas fácies teriam se colocado em função de quatro pulsos magmáticos (Wernick et al., 1993). Dantas (1990) indica que a colocação deste batólito é sincrônica à fase D2 de deformação das rochas encaixantes, ou algo posterior.

A idade do Maciço Cantareira, ou pelo menos de suas variedades porfiríticas dominantes, é de 630 ± 8 Ma, de acordo com Töpfner (1996, *apud* Azevedo, 1997, p.46). Esta idade corresponde, como proposto em trabalhos anteriores, àquela que definiria a colocação dos granitoides considerados “sin-tectônicos”.

O Maciço Taipas localiza-se imediatamente a oeste do granito Cantareira, apresentando afloramentos descontínuos, rodeados por metassedimentos;

destacam-se, principalmente, três áreas ou bossas, como identificado por mapeamento de revisão de Azevedo (1997). A área total é de poucos km², reunidos previamente como uma única ocorrência de 5 km² (Dantas, 1990), integrada principalmente por fácies do tipo Pirituba (75%), acrescido nas suas porções norte e sul pelo tipo Hortolândia (10%) e Itaguaçu (5%). De maneira geral, as rochas apresentam textura porfiróide, de matriz média a grossa, e composição monzogranítica variando para termos ganodioríticos, tonalíticos e mais raramente monzodioritos, estes restritos às bordas. A biotita apresenta-se como máfico principal, seguido de hornblenda; os minerais acessórios são titanita, apatita e opacos (sulfetos, ilmenita e titano-magnetita), ocorrendo ainda zircão, allanita e turmalina. Segundo Azevedo (1997), as rochas que constituem estes três stocks são muito parecidas entre si, com aspecto maciço e de cor cinzenta. A presença esporádica de anfibólio, ao microscópio, indica que se trata de um granitoide de natureza cálcio-alcalina: possivelmente, um dos representantes cálcio-alcálicos da associação Cantareira definida por Janasi e Ulbrich (1991, 1992). Existe apenas uma idade K-Ar em biotita de 540 Ma para este granito (Cordani; Bittencourt, 1967). Com este dado o granitoide seria classificado como “pós-tectônico”, pelos critérios expostos em trabalhos anteriores. A mineralogia denota claramente a tendência cálcio-alcalina destas rochas, representando tipos menos evoluídos, até associados ao magmatismo que originou o batólito Cantareira. A idade neste caso deveria ser superior aos 600 Ma, a julgar pelas datações mais definitivas hoje divulgadas na literatura.

O **Maciço Tico-Tico** (Moraes Rego, 1933) ou Anhanguera (Penalva; Hasui, 1970), constitui uma elevação topográfica elipsoidal à NW da Vila Perus, com aproximadamente 11 km² de superfície, com forma elipsoidal e orientado segundo a direção W-E. Segundo Carneiro (1983), a rocha predominante apresenta granulação média a grossa, geralmente inequigranular, cor cinza clara com variações para bege, creme e avermelhada quando alterada. São sienos - a monzogranitos compostos basicamente de quartzo, microclínio, plagioclásio e biotita, sendo os minerais acessórios mais comuns a muscovita, granada, turmalina e zircão. Observa-se em partes uma tênue foliação pela orientação dos cristais de biotita. Ocorre ainda uma série de veios pegmatóides dobrados, de composição granítica,

com as suas porções centrais enriquecidas em turmalina e filmes marginais com muscovita na interface com as rochas encaixantes.

Os “**turmalina-granitos de Perus**” (Dantas, 1990; Azevedo, 1997) se distribuem sob a forma de várias bossas de pequenas dimensões, algumas ocorrências menores e uma série de veios e diques de turmalina pegmatitos associados. O nível erosivo do domínio São Roque foi o suficiente para exumar maciços de colocação mais profunda (como o Cantareira), mas não oferece evidências que permitam relacionar o nível de afloramentos destes pequenos corpos com os dos maciços vizinhos (Taipas e Cantareira).

Ainda segundo Azevedo (1997), nas bossas, em especial, é possível observar três fácies de turmalina granitos, separados por textura e tamanho de grão: a fácies bandada, a homogênea e a pegmatóide. A *fácies bandada*, a mais abundante nas bossas, é marcada pela alternância de bandas com níveis claros e escuros, principalmente por variações mineralógicas. A mineralogia mostra feldspato potássico e plagioclásio esbranquiçado, quartzo, turmalina e alguma granada. Estas bandas repetem-se ritmicamente, constituindo conjunto de várias dezenas de unidades. Em geral, apresentam deformações que formam sistemas de dobras bastante complexos. Estas bandas são frequentemente cortadas por veios e diques pegmatóides, posicionados ora de maneira concordante ou subconcordante, ora cortando perpendicular ou obliquamente o bandamento ígneo. A *fácies homogênea* era muito rara, mas a *fácies pegmatóide* era observada como importante nas bossas, constituindo bolsões de dimensões métricas a decamétricas (com granulação muito grossa, em especial dos feldspatos e turmalinas, mostrando cristais com dimensões por vezes decimétricas) e enriquecimento em minerais raros (turmalinas róseas, granadas, micas de Li, além de complexa mineralogia de minerais tardios com U e/ou Ba colocados intersticialmente ou cristalizados em superfícies de fratura; ver literatura em Azevedo, 1997). Esta fácies pegmatóide, com afloramento nas bossas, era caracterizada como a *fácies pegmatóide interna* por Azevedo (1997), contrariamente à *fácies pegmatóide externa*, que aparecia em veios e diques pegmatóides cogenéticos isolados distribuídos pela região.

As idades até agora determinadas não parecem combinar com as evidências geológicas e petrográfico-geoquímicas nesses turmalina-granitos. Cordani e Bittencourt (1967) determinaram idade K/Ar (em micas de Li) de 650 ± 20 e 640 ± 20

Ma neles, enquanto Teuppenhayn (1994, *apud* Azevedo, 1997, p.50) identifica uma idade U/Pb (em monazita) de 566 ± 6 Ma. As feições geológico-mineralógicas indicam que se trata de granitoides altamente evoluídos, provavelmente cristalizados próximos à superfície, e em regime supostamente pós-tectônico, feições, portanto, diferentes das apresentadas pelo vizinho batólito Cantareira (cristalizado em maior profundidade, de natureza menos evoluída, etc.). O magmatismo Cantareira, a julgar pelo primeiro conjunto de idades, poderia estar associado à geração dos “turmalina-granitos de Perus”, mas a idade U-Pb afastaria estes últimos do evento Cantareira.

I.3.2. Domínio Jundiáí

O compartimento denominado Domínio Jundiáí (Figura I.2) está localizado a norte da Falha Itú-Jundiuvira e a sul da Falha Jacutinga; tem a oeste a Bacia do Paraná. De acordo com Wernick et al (1996) esse domínio também é denominado Complexo Itapira/Amparo, enquanto Janasi e Ulbrich (1991, 1992) caracterizam esse embasamento pelos Complexo Piracaia e o Grupo Andrelândia-Itapira. O Complexo Piracaia se caracteriza por rochas supracrustais de alto grau metamórfico, o Grupo Andrelândia-Itapira por outras rochas do Proterozóico Médio com metamorfismo de médio e baixo grau. A ocorrência de plutons graníticos pós-orogênicos nesse domínio foi estudada inicialmente por Hasui et al (1978b) que agruparam esses corpos com características muito semelhantes a granitos tipo A e textura “rapakivi” usando a denominação de “Suíte Intrusiva Itu”, com o principal complexo magmático sendo o Batólito ou Complexo Itu. A existência de um cinturão pós-orogênico com granitos contrastantes como tipo-A e cálcio-alcálinos justapostos foram descritos por Vlach et al (1990), que reconheceram esse arco na vizinhança da borda da Bacia do Paraná. Wernick et al (1997) cunharam o conceito de Província Rapakivi Itu como o de uma série magmática presente em um sistema magmático “plurisserial” espalhado pelo sistema orogênico da Mantiqueira com idades ao redor de 590 Ma.

Segundo Janasi et al (2009) os principais corpos graníticos relacionados à Província Granítica Itu incluem quatro principais ocorrências, as dos batólitos

graníticos de Itu e Morungaba, a do sieno-granito de Atibaia e a do monzodiorito de Piracaia, além de satélites desses corpos maiores.

O **Granito Morungaba** foi mapeado em detalhe por Vlach (1993), que reconheceu seis unidades intrusivas (*plúton Areia Branca, Complexo Ouro Verde, plutons Jaguari Oriental, Jaguari Meridional e plúton Itatiba*). As estruturas típicas desses granitos indicam mistura e “mingling” de magmas graníticos com magmas básico-intermediários, com exceção dos plútons Oriental e Itatiba, mais homogêneos e compostos por biotita-monzogranito equigranular.

Segundo Galembeck (1997) o **Batólito Itu** aflora por aproximadamente 300 km² e é constituído de quatro inclusões principais: Itupeva, Cabreúva, Salto e Indaiatuba. O *plúton Itupeva*, localizado mais ao norte, é dominado por biotita-monzogranitos inequigranulares. Ele apresenta um zoneamento grosseiro de minerais máficos, que se amplifica para o centro do corpo, refletindo uma provável mistura com magmas mais básicos. O *plúton Cabreúva*, a unidade maior e mais homogênea, é dominado por biotita-sienogranitos avermelhados com textura grossa. O *Plúton Salto* apresenta textura característica rapakivi, além de enclaves microgranulares félsicos arredondados mostrando quartzo e fenocristais de K-feldspatos em contatos acentuadamente moldados dentro desses enclaves, interpretados por Galembeck (1997) e Janasi et al (2006) como resultado de mistura de magmas. Outra ocorrência de granito com textura rapakivi é descrita como um novo corpo de forma irregular, ao norte do Plúton Cabreúva, denominado *Plúton Indaiatuba*.

O **sieno-granito de Atibaia** é descrito por Melhem (1995) como um plúton mediano (~45 km²), homogêneo, consistindo de sieno-granito róseo maciço de textura grossa, mas que mostra uma variedade fortemente deformada nas bordas do corpo. Apresenta enclaves de granulação média a fina e elevado teor de minerais máficos, provavelmente devido a mistura com magmas contemporâneos básicos e mais primitivos.

O **monzodiorito de Piracaia**, descrito por Janasi (1986; ver também Janasi e Ulbrich, 1987 e Janasi et al, 2007), é plúton de dimensão menor (~30 km²), com intrusão controlada também por zona de falhamento NE, constituído por rochas de básicas a intermediárias (índice de coloração entre 25-40) e variação composicional

ampla (monzodiorito a monzonito). Rochas félsicas aparecem como pequenos corpos independentes concentrados nas bordas do plúton.

O **Granito Terra Nova** é um maciço pequeno em dimensão (~23 km²) que se posiciona no extremo sul do “Maciço Mediano de Guaxupé”. Ele possui forma grosseiramente triangular e alongada na direção NE. Esse plúton é intrusivo em metassedimentos e parte do contato SE é tectônico (Falha de Jundiuvira). Pode ser classificado como biotita-granito róseo, maciço, com textura equigranular média a grosseira. Entre os principais minerais formadores tem-se quartzo, feldspato alcalino, plagioclásio, biotita e também anfibólio sódico. Apresenta uma fácies cinza, orientada na borda, com hornblenda substituindo o anfibólio sódico (Janasi; Ulbrich, 1992).

1.3.3. Domínio Embu

O Domínio Embu é uma unidade central no Cinturão Ribeira (Figura 1.2), limitada a norte pela Falha Taxaquara e o Domínio São Roque, a sul pela Falha Cubatão e Domínio Costeiro, a oeste pela Falha da Figueira e Domínio Açungui e a leste com o Cinturão Araçuaí. Esse domínio é constituído predominantemente por rochas supracrustais metamorfizadas em grau variável. Hasui (1973) e Hasui et al (1976) distinguiram duas associações litológicas, o Complexo Pilar do Sul e o Complexo migmatítico Embu, o primeiro formado principalmente por rochas metassedimentares de baixo grau metamórfico, o segundo por xistos e gnaisses migmatíticos.

Granitos fortemente peraluminosos são abundantes no Domínio Embu, formando assim várias ocorrências menores, e mesmo batólitos expressivos, de idade Neoproterozóica. Janasi et al (2003) indicam a participação predominante ou exclusiva de material derivado de crosta continental, sugerida pelo caráter fracionado das fácies dominantes, ou, em casos de rochas ricas em máficos, pelo caráter francamente peraluminoso das rochas.

O **Granito Itaquera** é uma dessas suítes graníticas na região leste da cidade de São Paulo (Janasi; Ulbrich, 1992). Cordani e Kawashita (1971) dataram essa

suíte granítica em 600 ± 90 Ma (método Rb-Sr). Hasui et al (2012) consideram o Granito Itaquera como um corpo pré- a sin-tectônico de idade Neoproterozóica (650-590 Ma) das unidades granitoides do tipo S, I, A gnaissificadas ou não. Abaixo é fornecida referência sobre nova idade deste granitoide. A rocha foi comercializada como Granito Itaquera em pedreira hoje desativada. Segundo Del Lama et al (2009), trata-se de um biotita-muscovita monzogranito, com estrutura levemente orientada, textura inequigranular, com grande variação granulométrica que confere à rocha um aspecto mais heterogêneo e anisotrópico. Enclaves micáceos de pequenas dimensões são comuns. Os minerais constituintes do Granito Itaquera indicam que a rocha foi deformada e possivelmente alterada hidrotermalmente.

I.3.4. Complexo Costeiro: Domínio Ubatuba

O Complexo Costeiro é delimitado a norte pela Falha Cubatão e a sul pela linha de costa e ilhas vizinhas (Hasui et al, 1981). De acordo com Chiodi et al (1983) e Sobreiro Neto et al (1983), essa unidade é constituída por três conjuntos litológicos distintos representados por sequências gnaiss-migmatíticas, para-derivadas e granulíticas. As rochas granulíticas, segundo Chiodi et al (1983) são constituídas predominantemente por charnockitos e noritos que ocorrem associados aos gnaisses oftalmíticos e aos corpos graníticos presentes na área.

Batólitos graníticos como o de Natividade da Serra e o de Caraguatatuba, e corpos como o de charnockitos de Ubatuba são encontrados no âmbito desse domínio, sendo na maioria corpos graníticos porfíricos considerados tardi- a pós-tectônicos com composição álcali-cálcica (Janasi; Ulbrich, 1992).

Tassinari et al (2001) interpretam as rochas da região como ígneas com gênese relacionada aos processos magmáticos que invadiram as rochas metamórficas do Complexo Costeiro. As idades das rochas no Domínio Costeiro se situam no Neoproterozóico (600-650 Ma), com plutonismo tardi a pós-tectônico, de caráter charnockítico, a ~550 Ma (Tassinari; Campos Neto, 1988; ver novas idades, em referência citada mais abaixo).

1.3.4.1. Maciço Ubatuba

Neumann (1993) identifica na região de Ubatuba (leste do Estado de São Paulo) seis corpos lenticulares de charnoquitos, em geral em contato transicional com um hornblenda-biotita-granito. O corpo maior aflora em uma superfície de aproximadamente 250 km², com 50 km de comprimento e em média 5 km de largura; o segundo atinge no máximo 12 km² de superfície e os demais são menores que 3 km². Sobre o corpo maior é que se localiza a cidade de Ubatuba.

Os *charnockitos* são granitóides que contêm piroxênios, com granulação em geral grossa à média, e coloração característica cinza-esverdeada. Parte da matriz fina apresenta textura granoblástica, produto de recristalização. Os principais minerais são, em ordem de abundância, feldspato potássico, quartzo, plagioclásio, biotita marrom-avermelhada, anfibólio marrom, clinopiroxênios levemente esverdeados e ortopiroxênios suavemente amarronzados. Os minerais acessórios são óxidos de Fe-Ti, apatita, zircão e allanita. O quartzo como grãos xenomórficos alongados definem a foliação da rocha. O K-feldspato também se apresenta como cristais alongados com bordas de irregulares a arredondadas; mostra débeis linhas de pertitas. O plagioclásio, com composição de oligoclásio a andesina, mostra em alguns casos intercrescimentos antipertíticos, podendo aparecer também mirmequitas ao longo das bordas com K-feldspato. O ortopiroxênio é xenomórfico e em parte alterado para massas de filossilicatos esverdeada ao longo das fraturas e clivagens. Hornblenda e biotita estão comumente associadas a piroxênios.

Os *biotita-granitos*, que em geral fazem contato com os charnockitos, tem mineralogia similar, mas sem piroxênios. Apresentam-se geralmente mais foliados, com desenvolvimento de grãos maiores de quartzo. Os feldspatos são bastante homogêneos, o potássico mostrando por vezes geminação em grade de microclínio.

1.3.4.2. Ilha Anchieta

Um corpo de biotita-hornblenda granito porfirítico constitui a maior parte da Ilha Anchieta. Relações de campo mostram que se trata de ocorrência intrusiva em charnockitos e granitos félsicos, com foliação tectônica bem desenvolvida, correlacionáveis aos charnockitos Ubatuba (idades U-Pb em 565 Ma determinadas por Azevedo Sobrinho et al, 2011). Segundo esses autores, a fácies petrográfica típica desses granitos tem índice de cor em torno de 15, composição modal variando de monzogranito e granodiorito a quartzo monzonito, com megacristais de microclínio tabulares (dimensão máxima entre 3 e 4 cm), em matriz com granulação média. Enclaves microgranulares máficos estão presentes, além de biotita e hornblenda; os minerais acessórios são zircão, titanita, apatita, allanita e óxidos de Fe-Ti, e os secundários incluem actinolita, epidoto e carbonato. Outras variedades de expressão local incluem uma fácies observada na borda oeste, ao longo do contato com os charnockitos encaixantes, com aspecto traquitoide por foliação de fluxo marcada pelo alinhamento de cristais de feldspato alcalino, e variedades félsicas, de aspecto aplítico, que aparecem como diques intrusivos na fácies principal.

Dados obtidos recentemente (Janasi et al., 2015; ver também discussão na Parte III) mostram que as idades dos granitos devem ser ajustadas. Foram determinadas idades de intrusão em torno de 598 e 591 Ma para rochas do Cantareira, 598 Ma para Taipas e Tico-Tico, e de 598 e 595 Ma para Itaqui, em geral mais jovens que as citadas anteriormente na literatura (ver citações acima). Da mesma maneira, idades obtidas para Itu (591 Ma), Itaquera (593 Ma) e charnockitos de Ubatuba (582 Ma) mostram-se também mais jovens que as listadas anteriormente na literatura, indicando que as diferenças entre manifestações sin- e pós-tectônicas, aparentemente, devem ser reduzidas a poucos milhões de anos.

I.4. OBJETIVOS E CONSIDERAÇÕES SOBRE APRESENTAÇÃO DOS RESULTADOS

Granitos são os constituintes mais abundantes da crosta continental, mas a diferenciação crustal reflete processos tanto sedimentares como também os magmáticos. Os granitos são gerados pelos processos de diferenciação magmática e/ou fusão de rochas de diversas fontes crustais. As Interpretações petrogenéticas dependem fundamentalmente de dados geológicos, petrográficos, mineralógicos e geoquímicos de boa qualidade e consistentes para que possam ser integrados, fundamentando possíveis modelos evolutivos.

Este trabalho apresenta dados úteis e importantes em corpos graníticos selecionados, representativos das diversas intrusões que afloram na faixa metamórfica Ribeira do Estado de São Paulo, com a finalidade de se observar regularidades, afinidades ou mesmo discrepâncias entre esses corpos intrusivos, permitindo discutir possíveis modelos evolutivos, com utilização de metodologia analítica moderna.

O aprofundamento do conhecimento sobre alguns desses corpos granitóides é baseado em análises petrográficas e mineralógicas dos granitos amostrados, complementadas com investigações geoquímicas pelas técnicas de Fluorescência de Raios-X (FRX) e espectrometria de massa com plasma indutivo acoplado (ICP-MS), bem como alguns dados isotópicos das razões Sm-Nd e Rb-Sr por espectrometria de massas por ionização térmica (TIMS), também em rocha total. Investigação geoquímica em zircões pela técnica de ablação a laser associada a espectrometria de massa com detector quadrupolo e plasma indutivo acoplado (LA-Q-ICPMS) e razões isotópicas U-Th-Pb por SHRIMP (Sensitive High Resolution Ion Microprobe) e Lu-Hf por LA-HR-ICPMS (Laser Ablation - High Resolution -ICPMS) são também tópicos importantes deste trabalho.

Aplicando-se as estratégias analíticas (descritas na Parte II), foram atingidos objetivos específicos com resultados preliminares, em parte ainda não publicados e discutidos na Parte III deste trabalho, como Anexos, citados a seguir.

Anexo A: An examination of selected granitoids occurrences in the São Paulo Ribeira Belt: trace element abundances in zircon as petrogenetic indicators.

Trata-se de texto a ser submetido ao Journal of South American Earth Sciences. Neste trabalho são descritos os principais resultados obtidos tanto nas determinações mineralógicas quanto analíticas em rocha total, bem como de elementos traço em minerais de zircão. A partir dos dados obtidos são discutidos alguns tópicos importantes sobre a possível gênese desses corpos graníticos intrudidos na Faixa Ribeira.

Anexo B: Methodology for the Determination of Trace and Minor Elements in Minerals and Fused Rock Glasses with Laser Ablation Associated with Quadrupole Inductively Coupled Plasma Mass Spectrometry (LA-Q-ICPMS).

Andrade et al (2014). Trata-se de artigo publicado no American Journal of Analytical Chemistry, apresentando a implantação de metodologia analítica para determinação de elementos traço em minerais e vidros silicáticos utilizando-se a técnica e ablação a laser associada à espectrometria de massa com plasma indutivamente acoplado utilizando discriminador de massa quadrupolo. Serviu de fundamentação para a implantação de rotina analítica para determinação de elementos traço em minerais de zircão.

Anexo C: Timing and sources of granite magmatism in the Ribeira Belt, SE Brazil: insights from zircon in situ U-Pb dating and Hf isotope geochemistry in granites from the São Roque Domain. Janasi et al (2015). É referência a artigo publicado no Journal of South American Earth Sciences. Nele são apresentados dados recentes de idades de corpos graníticos colocados no Domínio São Roque (sensu lato) da Faixa Ribeira, obtidos em zircão pelas técnicas de SHRIMP e LA-HR-ICPMS, além de dados de Lu-Hf nesse mesmo mineral para estes granitos. Os resultados são comparados com os obtidos pelas mesmas técnicas em zircão proveniente de sequência sedimentar metavulcânica *Statherian-Calymmian* (1.8-1.4Ma) da margem passiva do Domínio São Roque e de sua inferida fonte de crosta continental do período Arqueano-Paleoproterozóico.

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PARTE II - MATERIAIS E MÉTODOS

O componente experimental deste estudo consiste em uma abordagem sequencial de diversos métodos analíticos, que incluem desde análises petrográficas, mineralógicas, geoquímicas e isotópicas em rocha total até as determinações geoquímicas e isotópicas em zircão. Essa abordagem tem a finalidade de caracterizar os corpos graníticos amostrados e, principalmente, contribuir com informações novas sobre a possível gênese e idade da rocha granítica, bem como sobre os aspectos tectônicos controladores de sua colocação, em parte focalizando o mineral acessório zircão, que em geral traz gravado em sua estrutura composicional informações importantes sobre estes aspectos.

A seguir são descritos os principais métodos analíticos utilizados e detalhes sobre equipamentos e materiais de calibração.

II.1. QUÍMICA DE ROCHA TOTAL

II.1.1. Determinação de elementos maiores, menores e traço por FRX

A técnica de Fluorescência de Raios X (FRX) foi utilizada para determinação dos elementos maiores, menores e alguns elementos traço em rocha total.

As etapas de cominuição das amostras, que precede a determinação por FRX, foram baseadas em Sertek et al (2014). Foram utilizados cerca de 6 a 8 kg de rocha granítica, que foram fragmentadas em pedaços com cerca de 3-5 cm utilizando marreta ou prensa hidráulica. A seguir, eles foram britados para fragmentos com tamanhos médios de 1,5 cm em britador com mandíbula de aço-Mn. O material então foi dividido com quarteador cruzado tipo Jones, rendendo porções de 100 a 150 g de fragmentos representativos do material inicial. A primeira subamostra foi então submetida por 15 minutos a moinho planetário do tipo

Pulverisette, contendo anéis e cilindros de ágata. Esse tempo em geral é o suficiente para que o material atinja granulometria menor que 200 mesh (0,064 mm, ou menores). As demais subamostras foram reservadas para separação de zircão e determinações isotópicas nesse mineral.

Após obtenção do pó, as amostras foram levadas ao preparo das pastilhas fundidas, com mistura de boratos de lítio, para a determinação de elementos maiores e menores, e de pastilha prensada com cera do tipo *wax* ($C_6H_8O_3N_2$) para os elementos traço. A metodologia usada nas determinações por Fluorescência de Raios X está descrita em Mori et al (1999), efetuada em espectrômetro Phillips, modelo PW2400 com amostrador automático e tubo de molibdênio, no Laboratório de Fluorescência de Raio X do Núcleo de Apoio à Pesquisa em Geonálitica (NAP-Geoanalítica) do IGc-USP. Para o preparo das pastilhas fundidas utilizou-se 1 g de amostra e 9 g de mistura de tetra e metaborato de lítio de grau espectroscópico. A mistura foi fundida a temperatura de 1100-1200° C, em cadinho de platina-ouro, utilizando-se máquina de fusão Claisse modelo M4. O material foi então vertido em molde de 40 mm, também de platina-ouro, e resfriado para obtenção do vidro. A pastilha prensada foi obtida por mistura de 7 g da amostra pulverizada, previamente micronizada em equipamento modelo Micronizer da McCrone, e após seca, homogeneizada com cera e prensada em disco de 40 mm a 30 kPa usando prensa da Herzog.

II.1.2. Determinação de elementos terras raras (ETR) e outros elementos traço por ICP-MS

A metodologia usada na determinação dos elementos terras raras e outros elementos traço pela técnica de ICP-MS é descrita em Navarro et al (2008), com as determinações realizadas em espectrômetro de massa com plasma indutivamente acoplado, com analisador quadrupolo, modelo iCap da empresa Thermo-Fisher Co., disponibilizado no Laboratório de Química e ICP-MS do NAP-Geoanalítica no IGc-USP.

Cerca de 40 mg de pó de rocha com granulometria menor que 200 mesh foram colocados em cápsula de teflon de bomba Parr, adicionados 5 mL de ácido nítrico e 15 mL de HF, ambos destilados abaixo do ponto de ebulição (*“sub-boiling”*). A mistura ácida com o pó de rocha foi aquecida a 200° C em estufa elétrica, em pressão de 5-7 bar, por cinco dias. Após esse período o material resfriado foi transferido para béquer de PFA. A solução foi então aquecida em chapa elétrica para eliminação de SiF₄ gasoso por evaporação. Após secagem o material foi dissolvido e transferido para frasco plástico, onde o peso foi ajustado para 100g com HNO₃ 1%.

Detalhes sobre a calibração do espectrômetro de massa e tratamento dos dados analíticos podem ser obtidos em Navarro et al (2008).

II.1.3. Determinação de Sm/Nd e Rb/Sr

Análises isotópicas de Sr em amostras de rocha total foram realizadas no Centro de Pesquisas Geocronológicas do IGc-USP (CPGeo), baseadas na metodologia descrita por Sato et al (2008). O ataque das amostras foi semelhante àquele utilizado para o ICP-MS, com diferenças relacionadas ao tempo de digestão (10 dias a 160° C) em bomba Parr. Para as etapas de separação isotópica foram empregadas colunas de troca catiônica com resina AG-50W-X8 (200-400 mesh), usando água deionizada e HCl submetido também a destilação *“sub-boiling”* em concentrações variáveis. A extração do Sr foi realizada com HCl 2,5 N e o resíduo dessa etapa foi lavado com HCl 6,2 N para extração dos ETRs. A separação de Sm e Nd foi efetuada na alíquota de HCl 6,2 N a partir de colunas preenchidas com pó de teflon e lavagens sucessiva com HCl 0,26 N para separação do Nd e HCl 0,55 N para extração do Sm.

As determinações isotópicas de Sr foram realizadas em espectrômetro de massa com termo-ionização (TIMS), modelo TRITON da Thermo Scientific, e as de Nd em espectrômetro de massa com plasma indutivo acoplado, modelo Neptune da Thermo Scientific. As concentrações absolutas de Sm e Nd foram determinadas por

Q-ICPMS (espectrômetro de massa com analisador quadrupolo e plasma induzido acoplado) e as de Sr e Rb por FRX.

As razões normalizadoras são $^{86}\text{Sr}/^{87}\text{Sr} = 0.1194$ e $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, com constantes de decaimento dadas em Steiger e Jäeger (1978) e Michard et al (1985) para Sr e Nd, respectivamente.

No período de análise o branco de Nd foi de 61 pg e o de Sr de 142 pg. A reprodutibilidade externa de Sr foi testada por análises do material de referência NBS-987 do NIST-USA, que rendeu a relação de $0,710243 \pm 0,000024$, comparado ao valor certificado de $0,71034 \pm 0,000026$. A reprodutibilidade externa de Nd foi checada pelo material de referência JNdi-1 (Tanaka, 2000) e no período de análises forneceu relação $^{143}\text{Nd}/^{144}\text{Nd}$ de $0,512097 \pm 0,000005$. Para o cálculo de épsilon (ϵ) de Nd utilizaram-se os valores de ($^{143}\text{Nd}/^{144}\text{Nd}$) CHUR de 0,512638 e de ($^{147}\text{Sm}/^{144}\text{Nd}$) CHUR de 0,1967 (Hamilton et al, 1983).

II.2. QUÍMICA DO MINERAL ZIRCÃO

O zircão, um silicato de zircônio, se apresenta como mineral acessório em rochas ígneas e metamórficas, predominando em litotipos félsicos a intermediários. Trata-se de um mineral muito refratário que resiste aos mais variados ambientes geológicos. Ele é estável a elevadas temperaturas ($\sim 800^\circ\text{C}$), mas pode perder Pb no processo de metamictização, o resultado de danos no retículo cristalino causados durante a liberação de partículas subatômicas nos decaimentos radioativos de U e Th para Pb. Quanto maior a quantidade de U e Th existente nos cristais de zircão, e quanto mais antigo for o mineral, maior será o grau de metamictização. Nesse processo, canais abertos propiciam o escape de Pb radiogênico, permitindo também uma pequena entrada de Pb comum no sistema (Lee et al, 1997). Durante a cristalização do zircão a quantidade de Pb primário incorporado é muito pequena porque ele não é compatível com a estrutura desse mineral. O zircão é reconhecido por ser um transportador de um número elevado de isótopos radioativos e de seus produtos de decaimento, citando-se entre os principais os isótopos radioativos ^{238}U ,

^{235}U , e ^{232}Th , os quais decaem respectivamente para ^{206}Pb , ^{207}Pb , ^{208}Pb , contando-se ainda o ^{176}Lu , que decai para ^{176}Hf .

II.2.1. Separação do zircão e imagens de catodoluminescência

Os processos para separação e concentração dos minerais de zircão normalmente consistem de britagem, moagem e peneiramento, seguidos pela separação dos minerais pesados em mesa vibratória, separação eletromagnética, por líquidos densos e, por último, catação manual. A rotina utilizada no CPGeo-IGC-USP, onde foram realizadas essas análises, foi descrita por Sato et al (2014) e é constituída das seguintes etapas: **a.** a rocha bruta (0,5 a 3 kg para granitóides e ~20 kg para rochas máficas) é triturada em um britador de mandíbulas; **b.** o material britado é peneirado para separar uma fração de granulometria entre 100 a 250 mesh; a seguir, utilizando-se moinho de disco e uma bateria de peneiras, todo o material é submetido a processo de cominuição e separação por peneiramento; **c.** a fração separada é submetida a uma mesa vibratória do tipo “Wiffley” para concentrar minerais pesados tais como zircão, baddeleyita, titanita, monazita, apatita, etc.; **d.** do concentrado mineral obtido na etapa anterior, totalmente seco, são separados os minerais magnéticos, tais como magnetita e pirrotita, utilizando-se ímã de mão; **e.** do material que sobra após a passagem do ímã de mão, separam-se os minerais com diferentes susceptibilidades magnéticas usando-se o separador magnético tipo Frantz, variando-se a inclinação e a intensidade do campo eletromagnético (por exemplo, com corrente de 0,5 A com inclinação frontal de 20° e lateral de 10° consegue-se eliminar a grande maioria dos minerais paramagnéticos, tais como biotita, piroxênio e anfibólio); **f.** a porção menos magnética ou não magnética é passada sucessivamente nos líquidos densos bromofórmio ($d = 2,85 \text{ g/cm}^3$) e iodeto de metileno ($d = 3,2 \text{ g/cm}^3$) com o intuito de separar zircão, baddeleyita e monazita de apatita, quartzo e outros minerais descartáveis. Caso seja necessário separar zircão de monazita ou titanita, o material ainda é passado novamente pelo Frantz. A eliminação de eventuais sulfetos ainda existentes é conseguida com ataque dessa fração mineral com os ácidos HCl ou HNO_3 . Após a obtenção dos grãos de zircão,

com ajuda de microscópio binocular (lupa), cerca de 100 grãos de zircão são separados por catação manual, montados em fita adesiva dupla face, e emblocados em resina do tipo epóxi. A seguir o bloco é lixado e polido até exposição da superfície fresca dos grãos de zircão presos na resina.

Para a análise de zircão, que apresenta múltiplas fases de crescimento, é imprescindível realizar um estudo prévio óptico com catodoluminescência (CL) de cada uma das amostras para se determinar a posição adequada do *spot* (furo) analítico durante as análises das razões U-Pb e Lu-Hf. Essas imagens foram obtidas, após uma cobertura de fina camada de ouro (2-3 nm) no bloco de montagem (*mount*) de grãos de zircão, no espectrômetro FEI Quanta 250 SEM e XMAX detector de CL (*Oxford Instruments*). As condições operacionais foram: voltagem de 15 kV, distancia de 16.9-17 mm, corrente no filamento do detector PMD (filamento de emissão=100 μ A), intervalo de magnificação de 95-250 vezes.

II.2.2. Datação U/Pb (SHRIMP e ELA-ICPMS)

Na geocronologia U-Th-Pb pode-se utilizar o SHRIMP (*sensitive high-resolution ion microprobe*), um espectrômetro de massa sequencial, de alta resolução, acoplado a uma microsonda iônica, que utiliza um feixe primário de íons (O_2^+) acelerado e colimado para atingir um alvo onde íons secundários são gerados. Esses íons secundários são acelerados através do equipamento e os vários isótopos de $^{254}UO^+$, $^{206}Pb^+$, $^{207}Pb^+$, $^{208}Pb^+$, $^{238}U^+$ e $^{254}ThO^+$ e $^{196}Zr_2O^+$, gerados pela amostra ou padrão de calibração em spots de 32 μ m, são medidos sucessivamente. As correções necessárias na técnica são efetuadas através de análises de materiais desconhecidos juntamente com materiais de referência com relação isotópica conhecida - metodologia conhecida como “*matrix-matched*” - para determinação de fatores específicos de calibração (Black et al, 2004). Utilizou-se o equipamento SHRIMP IIe, e o zircão Temora 2 como material de referência, com idade estimada em 416.78 ± 0.33 Ma (Black et al, 2004). Durante as análises, a cada 5 determinações analisou-se novamente o material de referência Temora-2 para

cálculo dos fatores de correção de Pb comum e de fracionamento a serem aplicados às amostras.

Analísaram-se de 15 a 20 grãos de zircão de cada uma das nossas amostras selecionadas (TAP-1, ITA-2, ITQ-2, CHA-1, TICO-2, CANT-6, ITU-14X e TN-2). Inicialmente foram analisadas por SHRIMP, pela metodologia implantada no CPGeo-IGc-USP e descrita em Sato et al (2014), as amostras CHA-1, ITQ-2, TAP-1 e ITA-2 em dois dias de sessão analítica. As demais amostras TICO-2, CANT-6, ITU-14X e TN-2 foram analisadas sete meses após a primeira etapa de análises. Esse intervalo entre as duas etapas de análises por SHRIMP se deveu a dificuldade na separação dos grãos de zircão, devido às diversas etapas de manipulação da amostra, bem como do agendamento do equipamento sempre muito concorrido, pois se trata do único equipamento na América Latina.

A técnica de Excimer Laser Ablation, associada à espectrometria de massa de alta resolução com plasma indutivo acoplado (ELA-HR-ICPMS), é outra técnica utilizada para determinação de razões isotópicas com elevada precisão e, por esse motivo, também indicada para as determinações de idade em zircão e outros minerais portadores de Th e U. Nesta técnica o material em análise é retirado sob a forma de micropartículas por um sistema de ablação a laser. A seguir, estas partículas são introduzidas em um plasma de argônio onde são quebradas, atomizadas e ionizadas, sendo posteriormente submetidas a um campo elétrico e magnético para separação das diferentes massas dos isótopos. No sistema de ablação, apenas as partículas de amostra na faixa de 10-100µm são as que podem ser transportados eficientemente em fluxos não turbulentos a distâncias de até 1 m (Arrowsmith; Hughes, 1998). Essa técnica também foi utilizada neste trabalho para a determinação de idades em minerais de zircão, realizadas nas dependências do CPGeo-IGc-USP, com utilização do Laser Excimer pulsado de ArF 193 nm (Photon Machine) com condições operacionais de 6mJ, 8,55J/ cm² (100%), 6Hz e 40 µm de spot. O material ablado foi carregado através de um fluxo de 0,9 L/min de argônio (Ar) em mistura com hélio (He) para o espectrômetro multicoletor HR-ICPMS, modelo Neptune da Thermo-Finnigan, operado a 926 W. Uma configuração mista de coletores Faraday para leituras em V (voltagem) e multiplicadores de íons (MIC's) para cps permitiu obter medidas simultâneas dos teores de ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb e ²⁰⁸Pb, ²³²Th, ²³⁸U, ²⁰⁴Hg e ²⁰²Hg. O sinal obtido para cada um dos isótopos foi

integrado durante 60 s de ablação a laser em cada ponto analisado. Para cada amostra foram obtidas duas planilhas, cada uma com 13 determinações, intercaladas por duas análises de branco para correção de ^{204}Pb , duas determinações do material de referência zircão GJ-1 (idade estimada $^{206}\text{Pb}/^{238}\text{U}$ de 599.8 ± 4.5 ; Jackson et al, 2004) para correção da razão U/Pb e Th/U, e duas determinações do Nist-612 para correção da razão $^{204}\text{Pb}/^{206}\text{Pb}$. As amostras SR-07, MD-24 e MD-42B foram especialmente selecionadas para se verificar a robustez das idades obtidas por SHRIMP, uma vez que as amostras MD-42B e MD-24 são, respectivamente, amostras de rochas satélites dos granitos Cantareira (Cant-6) e Itaqui (ITQ-2) e, por esse motivo, com idades muito similares as anteriormente obtidas pela técnica de SHRIMP.

Os dados obtidos com ambas as técnicas (SHRIMP e high resolution LAICP-MS) foram reduzidos com software SQUID 1.06 (Ludwig, 2009) e os diagramas de concórdia foram obtidos com ISOPLOT 4 (Ludwig, 2003).

II.2.3. Determinação dos isótopos de Hf pela técnica de ELA-ICPMS

As análises de Hf em zircão foram efetuadas utilizando o ICP-MS Neptune da ThermoFinnigan, um espectrômetro de massa multicoletor de alta resolução para medições simultâneas de razões isotópicas entre $^{173}\text{Yb}/^{171}\text{Yb}$, $^{179}\text{Hf}/^{177}\text{Hf}$, $^{176}\text{Lu}/^{177}\text{Hf}$ e $^{176}\text{Hf}/^{177}\text{Hf}$. Utilizou-se como amostrador o Laser Excimer pulsado de ArF 193 nm (Photon Machine) com condições operacionais de 6 mJ, 8,55 J/cm² (100%), 7 Hz e spot de 47 µm. O material ablado foi carregado para o plasma, operado a 1000 W, através de um fluxo de Ar de 0,5 L/min, 0,25 L/min de He e 1,2 L/min de N₂. Os valores medidos da razão $^{176}\text{Hf}/^{177}\text{Hf}$ para o material de referência GJ-1 ficaram em torno de 0.282063 ± 0.000293 (n=4, 2 *sd*), em concordância com o valor de 0.282000 ± 0.000004 publicado por Morel et al (2008). Os resultados obtidos foram tratados em planilha Excel com 15 dados utilizando-se a constante de decaimento de $^{176}\text{Lu}=1,867\text{e-}11$ (Soderlund et al, 2004), e para cálculos dos εHf as razões $^{176}\text{Hf}/^{177}\text{Hf}=0,282772$ (CHUR), 0,283225 (DM); $^{176}\text{Lu}/^{177}\text{Hf}=0,0332$ (CHUR), 0,038512

(DM) e 0,015 para “*bulk Earth*” (Blichert-Toft ; Albarede, 1997, Vervoort; Blichert-Toft, 1999).

II.2.4. Determinação de elementos maiores, menores e traço em zircão por LA-Q-ICPMS.

A implantação da metodologia para a determinação de elementos menores e traço em zircão foi baseada nos trabalhos de Gao et al. (2002) e Yuan et al. (2008). Foi importante também a experiência desenvolvida no Laboratório de Química e ICP-MS (Andrade et al, 2010, 2014) na implantação de metodologia para análise de elementos traço em zircão em outros materiais de referência geológicos, tais como BHVO-2G, BCR-2G, BIR-1G, provenientes do USGS (2002) e nos vidros de rochas komatííticas GOR-128 e GOR-132G, de basaltos KL-2G e ML-3BG e do quartzo diorito T-1G, preparados pelo Max-Planck-Institut für Chemie da Alemanha (Jochum et al., 2005).

As análises foram efetuadas utilizando-se o equipamento de *Laser Ablation* modelo UP-213AF da New Wave/ESI com a célula de amostra modelo “*supercell*” e o espectrômetro de massa com analisador quadrupolo modelo Elan-6100DRC da PerkinElmer.

Devido à dificuldade em se obter materiais sintéticos de referência bem caracterizados do tipo zircão, optou-se por efetuar o teste da metodologia implantada por análise de materiais de referência naturais. Os materiais escolhidos e disponíveis foram os seguintes minerais de zircão: GJ-1 e 91500, já caracterizados e bem descritos na literatura, nas análises de razões isotópicas U-Th-Pb para datação, a maioria apresentando dados para os teores de elementos traço.

O zircão GJ-1, proveniente de um comerciante de gemas de Sidney, foi descrito inicialmente por Jackson et al (2004), e alguns dados para os teores dos elementos traço foram obtidos para os cristais com coloração vermelha por Yuan et al. (2008). O material de referência zircão 91500 é um único cristal com massa de 238 gramas, proveniente de Kuhel Lake (Ontário, Canadá), descrito e monitorado para teste de homogeneidade para idade U-Pb por “*secondary ion mass*

spectrometry” (SIMS) por Wiedenbeck et al (1995). A abundância de REE para esse zircão 91500 foi obtida por SHRIMP por Sano et al (2002), pelas técnicas de SIMS, e INAA por Wiedenbeck et al (1995, 2004) e, também, por LA-ICPMS, por Yuan et al (2004). O material utilizado nas análises deste trabalho foi obtido em 2013 pelo IGc-USP, tratando-se de pedaços do cristal inicial provenientes do segundo lote desse material de referência preparado e analisado por Michael Wiedenbeck em conjunto com o Harvard *Mineralogical Museum* em 2012 e que tem sido comercializado pelo *International Association of Geoanalysts* (IAGeo, 2015).

Para a calibração, controle de *drift* instrumental (variação das intensidades com o tempo numa mesma amostra) e do fracionamento, utilizou-se o material de referência na forma de vidro sintético SRM-610 do *National Institute of Standards* (NIST) com valores de referência fornecidos pelo próprio NIST e também no site do Georem (2005).

II.2.4.1. Metodologia analítica utilizada

Na metodologia de determinação de elementos traço em zircão pela técnica de LA-ICPMS, no tempo médio de 120 segundos, são analisados 34 elementos, cujos isótopos e dados de aquisição do sinal são fornecidos na Tabela II.1. Nos primeiros 60 segundos de análise são efetuados medidas de branco, que são leituras de todos os isótopos nas condições normais de análises, mas sem o acionamento do laser. Essas determinações são efetuadas na mistura do gás hélio, que passa pela cela de amostra do sistema de *laser ablation*, e do argônio, que provém do nebulizador do ICP-MS que se junta ao hélio por uma conexão em T para atingir o plasma. Esses dados de linha de base (*background*) são utilizados no cálculo do branco e dos limites de detecção e quantificação para cada elemento em cada uma das amostras. A análise de branco é apropriada porque leva em consideração qualquer contribuição além dos gases e do sistema que possa vir da célula onde são colocadas as amostras (e.g., contaminação das paredes dos tubos de transporte das partículas de amostras; efeito memória no sistema). Os 60

segundos seguintes são usados para aquisição de dados analíticos do material retirado pelo laser por ablação da amostra.

Os parâmetros instrumentais para o espectrômetro Elan-6100DRC da PerkinElmer, assim como para o sistema de Laser Ablation da New Wave UP-213/AF são também apresentados na Tabela II.1; os de aquisição de dados são fornecidos na Tabela II.2. Os dados são adquiridos no modo de busca do pico (*peak hopping*) com tempo de ajuste entre cada isótopo (*settling time*) de 2 ms, MCA igual a um, detector no modo dual (analógico e pulso) e modo padrão (ou *standard*, sem uso de células de reação ou colisão); o protocolo de aquisição de dados é do tipo tempo por intensidade (*time-resolved*) do software próprio do espectrômetro de massa. Esse protocolo de aquisição permite a aquisição de sinal como função do tempo e os resultados são reportados como intensidade do sinal (*cps*) versus tempo (s), permitindo reconhecimento de qualquer heterogeneidade na superfície analisada (modo de ablação do tipo trincheira: *raster*) ou do volume ablado (modo furo: *spot*).

Para as análises dos elementos traço, devido ao crescimento concêntrico oscilatório observado principalmente em zircão magmático, ou mesmo os setoriais em alguns tipos de zircão metamórfico ou simplesmente alterados por influência de fluidos, foram utilizados, principalmente, o modo *raster* de 80 µm com spot de 40 ou 30 µm e o passo do *raster* de 1-2 µm/s. O uso desse modo *raster* permite visualizar durante toda a análise a superfície do mineral que está sendo ablada, sem perda expressiva de sinal pelo aprofundamento do furo, ou aumento do fracionamento dos elementos retirados, já que o modo *raster* propicia abrir uma trincheira rasa (~ 10-20µm) que permite facilmente a saída do material ablado. A baixa velocidade de passo do *laser* também permite a formação de partículas menores durante todo o tempo de análise, o que influi bastante minimizando o fracionamento observado (detalhes em Kosler, 2008).

Os resultados obtidos são tratados em tempo real pelo software Glitter® (Van Achterbergh et al, 2001), que efetua *on-line* as correções do *drift* instrumental através do uso de padrão interno de um elemento previamente escolhido e de material de referência externo, além do cálculo dos teores dos elementos em análise. As equações matemáticas usadas para cálculos das concentrações dos elementos analisados, bem como os dados estatísticos (como limites de detecção, desvio padrão, etc.) são fornecidos em Jackson et al (2001) e Andrade et al (2014).

Tabela II.1. Parâmetros instrumentais utilizados na rotina para determinação de elementos maiores, menores e traço em zircão por LA-Q-ICPMS.

Parâmetros	Elan-6100 DRC (PerkinElmer)	Laser Ablation UP-213AF (New Wave)
Potência de RF	1350 W	
Gás Auxiliar (Argônio)	1 L/min	
Fluxo do Plasma (Argônio)	16 L/min	
Fluxo de gás Hélio	0,50 L/min	
transportador Argônio	0,48 L/min	
Distancia cone amostrador	4 mm	
Tipo do cone amostrador / abertura (mm)	Pt /1.1 mm	
Tipo do cone escumador / abertura (mm)	Pt / 0.9 mm	
varredura (<i>sweeps</i>) / leituras (reading)	1	
No. de replicatas	1	
Leituras (<i>readings</i>)	270	
Tipo de laser		Nd-YAG
Comprimento de onda		213 nm
Duração do pulso		5 ns
Taxa de repetição do laser		20 Hz
Densidade de energia		5-8 J/cm ²

Para a metodologia do zircão utilizou-se o material de referência NIST-610 como referência externa e testou-se o uso dos teores estequiométricos de SiO₂ (igual a 33%, proporção em peso) e ZrO₂ (como 67%) como valores do padrão interno calibrador no mineral zircão. Em geral, para outros minerais não estequiométricos os teores devem ser determinados por microsonda eletrônica; para o zircão, e outros minerais de composição estequiométrica, essa aproximação é amplamente utilizada na literatura (Liu et al, 2010). Os resultados obtidos com o uso de ambos os elementos calibradores são discutidos a seguir. O tratamento de dados *on-line* com esse software também permite a verificação dos teores de

background, sinal espectral (se existe inclusões ou mudanças abruptas nos teores dos elementos), qualidade analítica (DL, 1 sigma, etc.) e recálculos dos resultados em concentrações, normalizados pelo condrito, e gráficos associados.

A sequência de aquisição de dados para essa rotina está indicada abaixo: NIST-6102(a), NIST-610(b), NIST-610(c), Am(1),, Am (6), (QC-1), NIST-610(d), NIST-610(e), Am(7),, Am (14), (QC-2), NIST-610(i), NIST-610(j), NIST-610(h).

Tabela II.2: Analitos, massas dos isótopos e tempo de integração do sinal (*dwell time*)

Analito	Massa	Dwell time (ms)	Analito	Massa	Dwell time (ms)	Analito	Massa	Dwell time (ms)
Li	7	16,6	Nb	93	16,6	Ho	165	16,6
Mg	24	16,6	Mo	95	16,6	Er	166	16,6
Al	27	16,6	Ba	137	25,0	Tm	169	16,6
Si	29	16,6	La	139	25,0	Yb	173	16,6
P	31	16,6	Ce	140	16,6	Lu	175	16,6
Ca	44	16,6	Pr	141	16,6	Hf	179	16,6
Sc	45	16,6	Nd	143	16,6	Ta	181	16,6
Ti	49	16,6	Sm	147	16,6	Pb	208	25,0
Mn	55	16,6	Eu	151	16,6	Th	232	16,6
Sr	88	16,6	Gd	157	16,6	U	238	16,6
Y	89	16,6	Tb	159	16,6			
Zr	91	8,33	Dy	163	16,6			

Entre cada amostra é efetuada uma lavagem da cela de amostra por aproximadamente 60 s com o gás hélio, um procedimento que permite, além da limpeza da cela para a próxima amostra, uma estabilização do *background* mais rápida que utilizar o argônio. As leituras dos materiais de referência NIST-610 (a, b, c, d, e, f) são utilizadas como padrão interno e também para correção de *drift* ao longo do tempo de todo o procedimento analítico. Entre o aquecimento do sistema, com estabilização do *laser* e do plasma, e otimização das condições diárias de análise, o tempo total de análises é de quase 3 horas para 24 amostras.

Na Tabela II.3 são fornecidos os dados obtidos experimentalmente para limites de detecção dos elementos analisados nessa metodologia.

Tabela II.3. Médias, desvio padrão (s), desvio padrão relativo (% RSD) e número de determinações (n) dos limites de detecção (ppb).

Elemento	média	s	RSD(%)	n	Elemento	média	s	RSD(%)	n
Li7	2,27	0,48	21%	115	Sm147	0,37	0,09	25%	115
Mg24	1,24	0,31	25%	115	Eu151	0,12	0,03	28%	115
Al27	2,85	0,54	19%	115	Gd157	0,33	0,10	31%	115
Si29	527	86	16%	115	Tb159	0,05	0,02	31%	115
P31	38	7	18%	115	Dy163	0,22	0,07	34%	114
Ca44	283	46	16%	115	Ho165	0,06	0,02	27%	111
Sc45	0,73	0,13	18%	115	Er166	0,16	0,04	28%	114
Ti49	3,84	0,88	23%	115	Tm169	0,05	0,01	27%	114
Mn55	1,25	0,22	17%	115	Yb173	0,38	0,12	31%	114
Fe56	32	23	73%	115	Lu175	0,06	0,02	32%	112
Rb85	0,22	0,04	18%	115	Hf179	0,38	0,13	35%	115
Sr88	0,11	0,03	26%	115	Ta181	0,05	0,02	30%	115
Y89	0,08	0,02	25%	115	Pb207	0,51	0,12	23%	115
Nb93	0,10	0,03	27%	115	Pb208	0,29	0,06	21%	115
Mo95	0,80	0,22	27%	115	Th232	0,06	0,02	32%	115
Ba137	0,44	0,12	26%	115	U238	0,08	0,02	31%	115
La139	0,06	0,02	28%	115					
Ce140	0,07	0,02	27%	115					
Pr141	0,05	0,01	29%	115					
Nd143	0,44	0,13	30%	115					

Durante o período de análise não é necessário efetuar a correção de interferências nos isótopos escolhidos, já bem identificadas, tais como $^{28}\text{Si}^{17}\text{O}^+$, $^{27}\text{Al}^{18}\text{O}^+$ e $^{90}\text{Zr}^{2+}$ sobre ^{45}Sc , $^{131}\text{Ba}^{16}\text{O}^+$ sobre ^{151}Eu , e outras. As interferências de óxidos e hidróxidos são muito baixas no plasma seco devido à escassa presença de oxigênio e dos seus radicais O_2^- . A taxa de formação de óxido diário é monitorada pela formação do composto ThO , que em geral permanece abaixo de 1%. A formação de espécies duplamente carregadas também é reduzida quando se aperfeiçoa o fluxo de gases, mantendo-as abaixo de 3%.

II.2.4.2. Resultados obtidos para materiais de referência

Os dados apresentados a seguir foram obtidos para os materiais de referência zircão 91500 e zircão GJ-1 no espectrômetro ICP-MS modelo Elan-6100DRC como controles de qualidade analíticos em determinações rotineiras de diversos minerais de zircão. Os valores são apresentados nas Tabelas II.4 e II.5, respectivamente, para os materiais de referência zircão GJ-1 e zircão 91500, juntamente com os valores esperados para esses materiais. São apresentados os dados obtidos normalizados pelos valores estequiométricos de Si (ppm) e Zr (ppm). Quando se comparam os valores obtidos para cada um dos elementos analisados, utilizando-se esses dois elementos normalizadores, pode se observar que os resultados obtidos para Zr estequiométrico são sempre maior que os obtidos para Si como elemento normalizador, indicando um possível fracionamento diferente entre o elemento Si e os demais elementos, principalmente ETR. Dessa forma, deu-se preferência em comparar os dados obtidos com o elemento normalizador Zr e os valores recomendados. Nas Figuras II.1 e II.2 são apresentados os gráficos dos resultados obtidos divididos pelos valores recomendados para o zircão GJ-1 e 91500, respectivamente, calculados pelo elemento normalizador Zr estequiométrico. Como pode se observar, os resultados apresentam variação dentro dos limites de exatidão de $\pm 25\%$ do valor esperado, o que é amplamente aceito para materiais naturais que podem apresentar esse tipo de variabilidade.

Para o zircão GJ-1, os elementos com variação maiores que 25% são La, Pb, Th e U. O elemento La apresenta-se com valores abaixo do limite de detecção. O Pb fornecido é apenas do isótopo 208, enquanto o valor recomendado é para chumbo total. Como esse elemento apresenta variabilidade entre os percentuais dos isótopos dependendo do decaimento de Th e U, o ideal seria somar todos os isótopos para fornecer o valor de chumbo total; no entanto, o software de redução de dados Glitter® não permite essa manobra analítica. Os valores de Th e U, bem como de Pb, podem apresentar alguma variabilidade dentro da estrutura do zircão devido ao crescimento magmático e o decaimento radioativo.

Tabela II.4. Resultados obtidos para material de referência zircão GJ-1 para calibração com padrão interno %SiO₂ e %ZrO₂, e os valores de referência obtidos na literatura.

Isótopo	Dados obtidos experimentalmente no Laboratório										Dados recomendados (Liu et al, 2010)										Yuan et al (2008)	
	Calibrado para Si = 154255ppm					Calibrado para Zr= 496007ppm					fator		Calib. Zr= 496002ppm			Calib. Si = 154255ppm			fator			
	mediana	média	s	RSD		mediana	média	s	RSD	n	Si/Zr	média	2s	RSD	média	2s	RSD	Si/Zr	média	2s		
Si29	154255	154255				177058	173474	11806	7%	17	0.87	174533	812	0.2%	154255			0.88				
P31	64.9	51.0	29	56%		38.9	43.5	24.8	57%	17	1.67											
Sc45	163	165	13	8%		182	177	17	10%	17	0.90											
Ti49	3.87	3.98	0.80	20%		4.13	4.20	0.48	11%	17	0.94	3.55	0.29	4.1%	3.55	0.29	4.1%	1.00				
Mn55																						
Sr88	0.31	0.24	0.13	52%		0.097	0.095	0.030	31%	17	3.15											
Y89	255	243	35	15%		302	304	9	3%	17	0.84	246	1	0.2%	214	1.27	0.3%	0.87				
Zr91	431282	434564	16499	4%		496007	496007			17	0.87	496002			428490	1921	0.2%	0.86				
Nb93	8.7	8.7	0.3	4%		9.2	9.1	0.3	3%	6	0.95	1.51	0.02	0.7%	1.31	0.02	0.8%	0.87				
Mo95	7.0	7.0	0.2	2%		7.2	7.3	0.3	4%	6	0.97											
Ba137																						
La139	0.004	0.005	0.004	75%		0.004	0.007	0.004	64%	9	0.83	0.005	0.003	30%	0.005	0.003	30%	1.00	0.027	0.040		
Ce140	16.2	16.6	2.2	13%		19.4	18.7	2.4	13%	17	0.84	16	0.11	0.3%	14	0.098	0.4%	0.88	15.6	1.2		
Pr141	0.03	0.03	0.01	31%		0.030	0.030	0.007	24%	17	0.98	0.030	0.005	8.3%	0.027	0.004	7.4%	0.90	0.057	0.080		
Nd143	0.61	0.64	0.10	16%		0.67	0.65	0.08	12%	17	0.91	0.59	0.05	4.2%	0.51	0.04	3.9%	0.86	0.59	0.12		
Sm147	1.26	1.32	0.18	14%		1.42	1.43	0.14	10%	17	0.89	1.42	0.06	2.1%	1.24	0.05	2.0%	0.87	1.34	0.23		
Eu151	0.89	0.89	0.07	8%		0.98	0.95	0.12	13%	17	0.91	1.00	0.02	1.0%	0.86	0.02	1.2%	0.86	0.91	0.12		
Gd155	5.40	5.31	0.62	12%		5.92	5.95	0.55	9%	17	0.91	6.9	0.13	0.9%	5.98	0.12	1.0%	0.87	5.45	0.67		
Tb159	1.50	1.51	0.19	12%		1.66	1.66	0.12	7%	17	0.90	1.95	0.02	0.5%	1.68	0.02	0.6%	0.86	1.65	0.15		
Dy163	14.8	15.3	1.8	12%		17.2	16.6	1.0	6%	17	0.86	19.9	0.17	0.4%	17.2	0.17	0.5%	0.86	16.57	1.50		
Ho165	5.02	5.04	0.45	9%		5.44	5.46	0.35	6%	17	0.92	6.81	0.06	0.4%	5.90	0.06	0.5%	0.87	5.65	0.54		
Er166	21.1	21.4	1.5	7%		23.8	23.4	1.2	5%	17	0.89	29.3	0.19	0.3%	25.5	0.23	0.5%	0.87	23.75	2.30		
Tm169	4.66	4.75	0.34	7%		5.22	5.20	0.26	5%	17	0.89	6.25	0.05	0.4%	5.44	0.05	0.5%	0.87	5.20	0.49		
Yb173	49.4	49.6	3.2	6%		54.7	53.7	4.0	7%	17	0.90	62.0	0.47	0.4%	54.0	0.38	0.4%	0.87	53.8	5.6		
Lu175	8.40	8.57	0.77	9%		9.5	9.5	0.4	4%	17	0.89	12.4	0.08	0.3%	10.9	0.09	0.4%	0.88	10.29	1.09		
Hf179	4964	5267	525	10%		5752	5960	503	8%	17	0.86	7320	39.6	0.3%	6447	41.5	0.3%	0.88				
Ta181	0.31	0.32	0.05	15%		0.35	0.35	0.02	5%	17	0.89	0.44	0.01	1.1%	0.38	0.01	1.3%	0.86				
Pb208	0.81	0.80	0.11	14%		0.86	0.88	0.14	16%	17	0.94	34.5	0.18	0.3%	30	0.18	0.3%	0.87				
Th232	13.0	13.0	1.1	9%		14.6	14.3	0.8	6%	17	0.89	9.51	0.08	0.4%	8.25	0.08	0.5%	0.87				
U238	221	223	14	6%		259	252	25	10%	17	0.85	331	1.56	0.2%	287	1.69	0.3%	0.87	259	22		

Tabela II.5. Resultados obtidos para material de referência zircão 91500 para calibração com padrão interno %SiO₂ e %ZrO₂, e os valores de referência obtidos na literatura.

Isótopo	Dados obtidos experimentalmente no Laboratório										Dados recomendados		
	Calibrado para Si = 154255ppm				Calibrado para Zr= 496007ppm				N	fator	GEOREM		
	mediana	média	s	RSD	mediana	média	s	RSD			recom	s	RSD
Li7	2.96	3.10	0.71	23%	2.59	2.57	0.51	20%	18	1.20			
Mg24	0.90	0.90			0.63	0.68	0.20	30%	5	1.33			
Al27	8.51	8.80	1.53	17%	9.23	8.87	1.87	21%	24	0.99			
Si29	154255	154255			164196	163617	4037	2%	19	0.94	152600	1400	0.9%
Sc45	195	195	17	9%	192	194	15	8%	20	1.01			
Ti49	3.93	4.18	1.02	24%	4.24	4.51	1.38	31%	21	0.93	6.00	1	17%
Mn55					0.34	0.34			1	0.00			
Sr88	0.14	0.14	0.03	22%	0.14	0.13	0.03	23%	21	1.06	0.052	0.004	7.7%
Y89	116	116	8	7%	122	123	5	4%	16	0.94	150		
Zr91	437554	437500	23201	5%	496007	496007				0.88			
Nb93	2.46	2.53	0.25	10%	0.80	0.82	0.08	9%	11	3.08	0.79	0.07	8.9%
Mo95	2.44	2.37	0.51	22%	1.63	1.63	0.36	22%	11	1.45			
La139	< 0.06	< 0.06			< 0.06	< 0.06							
Ce140	2.36	2.36	0.21	9%	2.38	2.39	0.15	6%	19	0.99	2.60	0.3	12%
Pr141	<0.05	<0.05			<0.05	<0.05							
Nd143	<0.44	<0.44			<0.44	<0.44					0.24	0.04	17%
Sm147	0.44	0.46	0.12	27%	0.43	0.46	0.13	28%	17	1.01	0.50	0.08	16%
Eu151	0.19	0.18	0.05	28%	0.21	0.20	0.05	26%	27	0.88	0.24	0.03	13%
Gd157	1.69	1.75	0.29	16%	1.74	1.75	0.18	11%	20	1.00	2.20	0.3	14%
Tb159	0.65	0.62	0.08	13%	0.71	0.71	0.08	11%	28	0.88	0.86	0.07	8.1%
Dy163	8.43	8.59	0.81	9%	9.26	9.27	0.60	6%	24	0.93	12	1	8.3%
Ho165	3.73	3.63	0.23	6%	4.01	4.02	0.18	4%	24	0.90	4.80	0.4	8.3%
Er166	19.89	19.6	1.3	6%	20.9	20.9	1.2	6%	24	0.94	25	3	12%
Tm169	4.97	4.86	0.45	9%	5.18	5.21	0.39	7%	25	0.93	6.90	0.4	5.8%
Yb173	54.38	52.7	4.2	8%	58.2	58.4	3.9	7%	26	0.90	74	4	5.4%
Lu175	10.85	10.9	0.8	8%	11.8	11.8	0.7	6%	22	0.92	13	1	7.7%
Hf179	5673	5638	446	8%	5861	5907	364	6%	24	0.95	5900	300	5.1%
Ta181	0.33	0.32	0.05	16%	0.39	0.39	0.07	17%	26	0.82	0.50	0.1	20%
Pb207	3.99	3.94	0.62	16%	3.91	4.05	0.58	14%	26	0.97			
Pb208	2.56	2.50	0.26	10%	2.37	2.39	0.26	11%	17	1.05			
Th232	22.73	22.9	1.5	6%	24.1	23.9	1.5	6%	23	0.96	30.00	3	10%
U238	71.54	72.9	6.3	9%	73.0	73.2	3.6	5%	17	1.00	80.00	8.000	10%

Figura II.1. Gráfico dos dados obtidos para o material de referência zircão GJ-1 em comparação aos valores recomendados por Liu et al (2010).

Figura II.2. Gráfico dos dados obtidos para o material de referência zircão 91500 em comparação aos valores recomendados por Georem (2015).

Para o zircão 91500, os teores dos elementos traço e menores são, em geral, inferiores àqueles observados para o zircão GJ-1. Para ambos os materiais de referência, foram aqui analisados mais elementos que os que aparecem nas referências publicadas e, portanto, não existe possibilidade de fazer comparações; entretanto, todos os elementos aqui analisados, também citados na literatura,

aparecem com valores dentro dos limites de $\pm 25\%$ do valor esperado (recomendado), o que é bem aceito nesta técnica e por se tratarem de materiais naturais com variação química reconhecida.

Os dados obtidos permitem implantar a metodologia utilizando o teor estequiométrico de Zr como elemento calibrador do padrão interno. A utilização de silício leva a teores mais baixos para os resultados dos elementos menores e traço determinados. Essa diminuição é atribuída possivelmente a comportamentos diferentes entre o silício e os demais elementos terras raras, HFSE e zircônio, tanto durante a ablação a laser, quanto propriamente no plasma, caracterizado na literatura como fracionamento (Jackson, 2001).

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PARTE III - ASSINATURAS ISOTÓPICAS E ASPECTOS PETROGENÉTICOS DE GRANITOIDES DOS DOMÍNIOS EMBU, JUNDIAÍ E COSTEIRO.

III.1. CONSIDERAÇÕES INICIAIS

As rochas estudadas nesse trabalho são ocorrências complexas tanto do ponto de vista petrográfico quanto estrutural, ocorrendo como intrusões múltiplas com dimensões que variam de moderadas até batolíticas, e atinge até 30% da superfície exposta do embasamento no estado de São Paulo (Janasi; Ulbrich, 1991, 1992).

Nesta Tese se utilizaram as determinações multielementares em rochas e em minerais de zircão de granitoides presentes em várias unidades geológicas do Complexo Ribeira, no Estado de São Paulo, a fim de se identificar as similaridades e discrepâncias em teores de elementos traço. Este estudo teve como propósito observar padrões de evoluções petrogenéticas paralelas ou diferenciadas nas unidades cálcio-alcálinas e em seus derivados evoluídos.

Como uma linha adicional de evidências, foram determinadas as razões isotópicas nos sistemas U-Th-Pb e Lu-Hf em zircão, além das determinações isotópicas Sm-Nd e Rb-Sr em rochas (os dados de razões isotópicas e discussão sobre aspectos petrogenéticos e tectônicos para o Domínio São Roque são apresentados em publicação constante do ANEXO C, Parte IV, desta Tese; Janasi et al, 2015).

A seguir são fornecidos os dados para as razões isotópicas de algumas rochas dos Domínios Embu, Jundiaí e Costeiro (conforme definições em Janasi; Ulbrich, 1991, 1992) que foram avaliados neste trabalho.

III.2. RAZÕES ISOTÓPICAS Sm-Nd e Rb-Sr DE GRANITOIDES DOS DOMÍNIOS EMBU E COSTEIRO E COMPARAÇÃO COM OS DO DOMÍNIO SÃO ROQUE

Os dados obtidos neste trabalho para o Granito Itaquera (Domínio Embu) e o Charnockito Ubatuba são apresentadas na Tabela III.1.

Tabela III.1. Dados isotópicos de Rb-Sr e Sm-Nd para amostras ITA-2 e CHA-1.

amostra	plúton	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$ calc.	$^{87}\text{Sr}/^{86}\text{Sr}$ (medido)	erro (2s)	ϵ Sr t=600Ma	$^{87}\text{Sr}/^{86}\text{Sr}$ t=600Ma	Sr TDM (Ma)
ITA-2	Itaquera	290	117	7.153	0.776040	0.000052	156	0.71483	724
CHA-1	Costeiro	111	166	1.930	0.724750	0.000049	62	0.70824	823

amostra	pluton	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$ calculado	$^{143}\text{Nd}/^{144}\text{Nd}$ Medido	erro (2 σ)	ϵ Nd (0)	ϵ Nd t=600	f Sm/Nd	Nd TDM Ma
ITA-2	Itaquera	7.58	44.6	0.1032	0.511242	0.000006	-27.2	-20.1	-0.476	2458
CHA-1	Costeiro	11.4	54.8	0.1269	0.512136	0.000006	-9.8	-4.4	-0.356	1640

O Granito Itaquera (ITA-2) apresenta razão $^{87}\text{Rb}/^{86}\text{Sr}$ em torno de 7.15 e mostra que a idade Sr(TDM) de 724 Ma, calculada como único estágio, é compatível com as determinadas por Tassinari (1988) para o Granito Itaquera (7.26 e 722 Ma) e, também, similares ao dos granitos mais diferenciados do Domínio São Roque, entre eles o Tico-Tico (7.59). A razão $^{87}\text{Sr}/^{86}\text{Sr}$ (inicial) obtida também por Tassinari (1988) para o granito Itaquera foi de 0.7148, praticamente idêntica ao obtido neste trabalho (0.71483) e novamente comparável aos dados obtidos por Tassinari (1988) para o Granito Tico-Tico (0.717-0.720) pertencente ao Domínio São Roque, mostrando que ambas as rochas são evoluídas.

Os dados de Rb-Sr apresentados em Janasi et al (2015) para os granitóides do Domínio São Roque, trabalho já publicado e anexo a esta Tese (ver Parte IV), mostram para as amostras com teores de Sr superiores a 700 ppm (SR-07, São Roque; ITQ-2, Itaqui; MD-24, Fazenda Itahye - “satélite” do Itaqui), razões isotópicas de $^{87}\text{Rb}/^{86}\text{Sr}$ entre 0.2-0.5; naquelas com teores de Sr entre 300-700 ppm os valores dessa razão ficaram entre 0.6-1.6 (TAP-1, Taipas e MD-42B, “satélite” de Cantareira), em concordância com as obtidas por Tassinari (1988) e Ragatky

(1998). Cabe ressaltar ainda que em Janasi et al (2015) foram registradas idades de Sr(TDM) em único estágio, para granitos com elevado teor de Sr (HKCA, “*high K calc-alkaline*”) (São Roque, SR-07 e Itaqui, ITQ-1), valores maiores que 2 Ga, enquanto que para os corpos graníticos mais a leste, com teores intermediários de Sr (300-700 ppm), os valores registrados de idade Sr(TDM) são da ordem de 1-1.4 Ga (Taipas, TAP-1 e MD-42B, “satélite” de Cantareira), valores próximos aos encontrados por Tassinari (1988) para o Granito Cantareira.

Os granitos peraluminosos Tico-Tico e Pedra Branca do Domínio São Roque, com elevadas razões Rb/Sr (1.7-2.6), analisados por Tassinari (1988), registraram idades Sr(TDM) em torno de 0.70-0.83 Ga. Em função das linhas de evolução dessas rochas serem mais inclinadas em diagrama de evolução isotópica de Sr em função do tempo, Tassinari sugere que esses granitos são mais enriquecidos em ^{87}Rb e mais diferenciados do que Cantareira e Morro Azul. Ainda, de acordo com esse autor, os dados isotópicos de Sr e Pb permitem concluir que o magma parental do Granito Cantareira se diferenciou do manto superior cerca de 2.0 Ga atrás e, em torno de 700 Ma, sofreu processo de fusão parcial dessa crosta para cristalizar o granitoide em torno de 600 Ma, com razão $^{87}\text{Sr}/^{86}\text{Sr}_{(\text{inicial})}$ de 0.709-0.710. Essa razão isotópica $^{87}\text{Sr}/^{86}\text{Sr}_{(\text{inicial})}$ é coerente com as obtidas nesta Tese para os granitos Itaqui e Taipas; no entanto, eles apresentam idades Sr(TDM) diferentes entre si (2357 Ma e 1467 Ma, respectivamente).

Ainda segundo Tassinari (1988), alguns granitoides do Domínio São Roque mostram razões de $^{87}\text{Sr}/^{86}\text{Sr}_{(\text{inicial})}$ elevadas, que podem ser explicadas pela interação do magma granítico com a crosta superior. Essa mistura de magmas, gerada em níveis crustais profundos com fases líquidas contendo elementos incompatíveis, derivados de minerais hidratados da crosta continental superior, é uma das possibilidades para se elevar essas razões iniciais de Sr, como é o caso dos granitos Tico-Tico e São Roque que apresentam valores entre 0.713-0.720.

Para o Charnockito Ubatuba as razões $^{87}\text{Rb}/^{86}\text{Sr}$ e $^{87}\text{Sr}/^{86}\text{Sr}_{(\text{inicial})}$ de 1.93 e 0.7082, respectivamente, mostram que essa amostra teve proveniência em um protólito menos evoluído que aquele do qual teria sido gerado, por exemplo, o Granito Itaquera.

A relação Sm/Nd de rochas crustais não é modificada por eventos como metamorfismo, erosão ou redeposição (Faure, 1986). As idades modelo em Nd

podem ser interpretadas como o tempo de residência da rocha na crosta. Dessa forma pode se inferir pelos dados de Nd(TDM) que o magma parental dos granitos Itaquera (ITA-2), São Roque (SR-07) e Itaquí (ITQ-2) se diferenciou do manto superior a cerca de 2.0 Ga, assim como o Granito Cantareira (Tassinari, 1988). A amostra CHA-1 (charnockito) mostra uma idade modelo em torno de 1600 Ma e o $\epsilon Nd_{(0)}$ indica se tratar de uma rocha com protólito de idade fanerozóica.

III.3. RAZÕES ISOTÓPICAS U-Th-Pb E Lu-Hf DE GRANITOIDES DOS DOMÍNIOS EMBU, COSTEIRO E JUNDIAÍ E COMPARAÇÃO COM OS DO DOMÍNIO SÃO ROQUE.

Os dados das razões U-Th-Pb e Lu-Hf obtidos para os minerais de zircão dos granitos do Domínio São Roque (São Roque, Taipas, Itaquí, Tico-Tico, Perus e Cantareira) foram publicados em Janasi et al (2015), assim como os dados de datação para o granitoide Ilha Anchieta (IA-10D) em Azevedo Sobrinho et al (2011), com as respectivas discussões sobre as implicações petrogenéticas e tectônicas. A seguir serão apresentados os dados isotópicos de U-Th-Pb para as amostras de zircão dos granitos de Itaquera, Itu, Terra Nova e do charnockito de Ubatuba, e possíveis correlações com os granitos do Domínio São Roque, assim como os dados de Lu-Hf para essas amostras e também para Ilha Anchieta.

Os dados isotópicos U-Th-Pb para zircões do Granito Itaquera (amostra ITA-2) pertencente ao Domínio Embu, dos granitos Itu e Terra Nova (ITU-14X e TN-1), pertencentes ao Domínio Jundiá, e do charnockito Ubatuba (amostras CHA-1) do Domínio Costeiro, são apresentados na Tabela TS-1 (Dados Suplementares, Parte V), bem como os diagramas de concórdia com as respectivas idades de cristalização na Figura FS-1 (Dados Suplementares, Parte V). Imagens de catodoluminescência dos zircões analisados com os respectivos pontos amostrados são apresentados na Figura FS-2 (Dados Suplementares, Parte V).

A amostra ITU-14X teve 13 zircões amostrados por SHRIMP e utilizados para a obtenção da idade em 591 ± 28 Ma (MSWD de 1.18), através da interceptação da linha de concórdia, pois não foi possível obter um grupo coerente de amostras para

obtenção dessa idade. A amostra TN-1 teve 16 pontos de zircão amostrados por Shrimp usando o mesmo procedimento de interceptação da linha de concórdia para obter-se a idade provável de cristalização de 579 ± 12 Ma (MSWD = 0.38), devido também a impossibilidade de se obter um grupo coerente de amostras.

Na amostra ITA-2 do Granito Itaquera foram analisados por Shrimp 15 pontos e foram descartados três pontos devido aos elevados teores de chumbo comum (^{204}Pb) e também um zircão com elevado teor de U; a idade obtida por concórdia (91% de probabilidade) para os 11 pontos restantes foi de 593.5 ± 4.4 Ma (MSWM=0.013).

No charnockito Ubatuba (CHA-1) foram analisados por Shrimp 14 zircões e apenas um foi descartado devido à baixa relação Th/U. A idade concórdia para cristalização do granitoide foi de 582.4 ± 4.8 Ma (MSWM=0.013).

Comparando-se esses dados dos granitos do Domínio São Roque (amostras: Cant-6; MD-42B, "satélite" do Cantareira; SR-07, São Roque; ITQ-2, Itaqui; MD-24, "satélite" do Itaqui; TAP-1, Taipas; Tico-2) com os obtidos para as amostras Itu-14X (Itu), TN-1 (Terra Nova) e ITA-2 (Itaquera) se observa que as idades são muito próximas, com exceção de TN-1, possivelmente devido à discórdia entre os dados U-Th-Pb. O charnockito de Ubatuba, que também apresenta idade de cristalização menor que o grupo analisado, mostra coerência com os dados obtidos anteriormente por Heilbron; Machado (2003) para os terrenos sin-colisionais orientais do Domínio Costeiro, e por Gasparini; Mantovani (1979) para os leucogranitos associados ao Charnockito Ubatuba (~ 565 Ma), uma vez que tanto o granito de Ilha Anchieta (499.7 ± 5.9 Ma; Azevedo Sobrinho et al, 2011) como os leucogranitos são intrusivos no Charnockito Ubatuba.

Todos os zircões analisados para o domínio Embu, Jundiá e Costeiro mostraram idades de cristalização no intervalo de 594 a 579 Ma, sobrepondo-se as idades de cristalização dos granitos mais jovens (e.g. Tico-Tico, amostra Tico-2) e "satélite" Cantareira (MD-42B) do domínio São Roque, que variam de 594 a 590 Ma (Janasi et al, 2015).

Os dados de Lu-Hf obtidos em zircão por LA-HR-ICPMS para as amostras dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e Charnockito Ubatuba (CHA-1) são apresentados na Tabela TS-2 (ver Dados

Suplementares, Parte V). Os granitos do Domínio São Roque são descritos e discutidos por Janasi et al (2015; ver Parte IV).

A composição isotópica Lu-Hf foi obtida e avaliada para a amostra ITA-2 (Itaquera – Domínio Embu) pelo fator ϵ_{Hf} (594 Ma), que mostra uma estreita variação de 2 unidades de ϵ_{Hf} dentro do intervalo de -21.8 à -23.8, com média e desvio padrão de -22.7 ± 0.7 . Este valor é muito similar ao encontrado para a amostra SR-07 (São Roque-Domínio São Roque), com ϵ_{Hf} (603 Ma) de -21 à -24 e média de -22.8 ± 1.2 , valor próximo ao encontrado para a amostra ITQ-2 (-19 à -20), com média de -17.4 ± 1.4 , todas com característica de rochas derivadas de magmas crustais evoluídos (ϵ_{Hf} muito negativo). Para a amostra ITA-2, um zircão analisado mostrou $\epsilon_{\text{Hf}}(\text{T1})$ de -10.5, indicando possivelmente uma mistura com protólitos mais radiogênicos ou menos evoluídos, semelhantes ao encontrado para o enclave de Itaquí (ITQ-E), cujo ϵ_{Hf} (594 Ma) variou de -11 à -12.

As amostras TN-1 (Terra Nova) e ITU-14X, provenientes do Domínio Jundiá, mostram valores de ϵ_{Hf} (T1) muito próximos entre si: TN-1 de -8.3 à -13.3 (média de -10.8 ± 2.0) e Itu-14X de -8.1 a -14.8 (média de -11.3 ± 1.8) e, também, com uma ampla variação nos valores de ϵ_{Hf} (média de 5 unidades), indicando se tratar de fonte menos homogênea que as observadas para ITA-2 e SR-07. Nas amostras TN-1 e ITU-14X, alguns zircões analisados mostram valores de ϵ_{Hf} (T1) mais negativos que as médias determinadas para essas amostras (-16.8 e -17.7, respectivamente), indicando uma provável interação com protólitos mais evoluídos. Os dados de ϵ_{Hf} (T1) para as amostras TN-1 e ITU-14X estão no mesmo intervalo daqueles observados para as amostras de granitos provenientes do Domínio São Roque, MD-42B (“satélite” do Cantareira), TAP-1 (Taipas) e Tico-2 (Tico-Tico), cujos intervalos de variação do ϵ_{Hf} (T1) se encontram, respectivamente, na faixa de -9.5 a -12, de -10.5 a -14 e de -10.5 a -12. Em um zircão da amostra TN-1 foi encontrado ϵ_{Hf} (T1) de -0.48, indicando alguma interação com restitos mais radiogênicos.

As amostras de granitoides provenientes do Domínio Costeiro CHA-1 (charnockito) e IA-10D (Ilha Anchieta) mostram ampla variação do ϵ_{Hf} (T1), chegando a mais de 5 unidades de ϵ_{Hf} para o Charnockito de Ubatuba (-2.2 à -6.7, média de -4.4 ± 1.3), enquanto para IA-10D os valores estão na faixa de -4.3 à -7.8 (média de -6.2 ± 1.2). Em ambas as amostras observa-se um caráter crustal menos evoluído

quando comparados às demais amostras, principalmente para o Charnockito Ubatuba, indicando alguma mistura com fontes mais mantélicas e radiogênicas.

Para uma discussão das possíveis fontes dos granitos estudados nesta Tese serão consideradas as razões de Lu/Hf comumente utilizadas na literatura para a crosta intermediária (0.015) (Vervoort et al, 1999). Na Tabela III.2 é apresentado um resumo das idades obtidas através dos dados isotópicos de U-Th-Pb, dos valores de ϵ_{Hf} (T1) e idade TDM obtidos pelo método de Lu-Hf, além dos dados de ϵ_{Nd} (T1) e idade TDM obtidas através das razões Sm/Nd para as amostras do Domínio São Roque, Embu, Jundiaí e Costeiro. Na Figura III.1 pode ser visualizado o diagrama de ϵ_{Hf} versus tempo (Ma) para os granitos São Roque, Taipas, Tico-Tico e Satélite Cantareira do Domínio São Roque, Terra Nova e Itu do Domínio Jundiaí e Itaquera do Domínio Embu, além da curva para o manto empobrecido. A extrapolação das curvas de evolução para o tempo anterior à geração dos granitos foi calculada utilizando o valor para a relação $^{176}\text{Lu}/^{177}\text{Hf}$ de 0.015, que corresponde a crosta intermediária.

Figura III.1. Diagrama de ϵ_{Hf} versus tempo para os granitos São Roque, Taipas, Tico-Tico e satélite Cantareira do Domínio São Roque, Terra Nova e Itu do Domínio Jundiaí e Itaquera do Domínio Embu.

A Figura III.2 apresenta o diagrama de ϵ_{Hf} versus tempo para os granitoides provenientes do Domínio Costeiro.

Tabela III.2. Dados isotópicos U-Th-Pb e Lu-Hf, e idades calculadas para as amostras dos granitos provenientes dos Domínios São Roque, Embu, Jundiá e Costeiro.

Dominio / maciços	idade Ma		Dados Lu-Hf				εNd(600)	Idade Nd(TDM) Ma
	valor médio ± 2s		εHf (T1) valor médio ± 1s		Idade TDM (Ma) valor médio ± 1s			
São Roque								
São Roque (SR-07)	602.6	1.9	-22.8	1.2	2927	80	-15.0	2152
Itaqui (ITQ-2)	594.1	6	-17.4	1.4	2595	80	-12.1	1941
Itaqui enclave (ITQ-E)			-16.0	3.4	2526	218		
Taipas (TAP-1)	598.0	7.2	-11.9	1.2	2243	81	-9.8	1780
Faz. Itahye (MD-24)	598.1	1.8	-16.9	1.4	2559	95	-11.1	1890
Tico-Tico (Tico-2)	602.6	4.3	-11.4	0.7	2205	29		
Cantareira (Cant-6)	598.3	3.1	-16.5	1.8	2531	98		
"Satelite" Cant. (MD-42B)	591.8	1.9	-11.1	1.3	2167	51	-9.0	1645
Granito Perus (Pe-04)			-18.1	2.0	2653	89		
Embu								
Itaquera (ITA-2)	593.9	5.8	-22.7	0.7	2910	41	-20.1	2458
Costeiro								
Charnockito (CHA-1)	581.7	4.8	-4.4	1.3	1757	88	-4.4	1640
Ilha Anchieta (IA-10D)	499.7	5.9	-5.9	1.5	1787	103		
Jundiá (Província Itu)								
Itu (ITU-14X)	591	28	-11.6	2.0	2198	102		
Terra Nova (TN-1)	579	12	-11.1	2.0	2160	123		

A análise dos dados da Tabela III.2 e do diagrama da Figura III.1 indica que as idades modelo (TDM) originadas das razões Lu-Hf para as amostras provenientes dos domínios São Roque, Embu e Jundiá distribuem-se num intervalo de tempo entre 2.2 e 2.9 Ga. As amostras SR-07 e ITA-2 provenientes dos domínios São Roque e Embu, respectivamente, apresentam uma fonte Paleoproterozóica comum de 2.9 Ga e com ϵHf de -22.8, indicando tratar-se de uma fonte com elevada residência crustal, conforme já discutido em Janasi et al (2015). Esses resultados são corroborados pelos obtidos por Sm-Nd que mostram idades TDM entre 2.2 e 2.5 Ga representando uma fonte crustal que pode estar possivelmente associada a Paleoplaca São Francisco (Janasi et al, 2015).

Os granitos Itu e Terra Nova provenientes do Domínio Jundiá necessitam de uma fonte mais radiogênica para explicar os valores menos negativos para ϵHf e ϵNd (-12, -9), assim como os granitos peraluminosos e subalcalinos do Domínio São Roque como, por exemplo, o Granito Tico-Tico, o qual revela através de núcleos

herdados de zircão idades entre 1.5 a 1.8 Ga. Essas fontes poderiam ser crostas juvenis formadas em 1.75 Ga, durante evento de vulcanismo dentro de placa tectônica devido à abertura continental (*rifting*), conforme discutido em Janasi et al (2015).

Figura III.2. Diagrama de ϵ_{Hf} versus tempo para os granitoides do Domínio Costeiro (CHA-1, charnockito e IA-10D, granito Ilha Anchieta) em comparação com ITA-2 e ITU-14X do Domínio Jundiá e amostras Cant-6 e TN-1 do Domínio São Roque.

As amostras de granitoides do Domínio Costeiro CHA-1 (charnockito) e IA-10D (Ilha Anchieta), apresentadas na Figura III.2 e Tabela III.2, mostram pelos dados de $\epsilon_{\text{Hf}}(T_1)$, idade modelo de $\text{Hf}(\text{TDM})$, $\epsilon_{\text{Nd}}(T_1)$ e idade modelo de $\text{Nd}(\text{TDM})$ que elas possuem em comum, provavelmente, um protólito bem mais juvenil que as amostras ITA-2, Cant-6, ITU-14X, e TN-1, ou seja, com menor tempo de residência crustal, provavelmente mostrando uma possível influência de fontes mais radiogênicas, e até mesmo mantélicas. Azevedo Sobrinho et al (2011) chama a atenção para enclaves microgranulares máficos de formas elípticas que aparecem no granito de Ilha Anchieta e apresentam evidências de interação desse enclave com o granito. O charnockito Ubatuba mostra um caráter mais aluminoso, típico de magmas mais anidros e quentes, observados em ambientes tectônicos sin-colisionais, contrastando com corpos derivados de fontes mantélicas típicos de ambientes tectônicos extensionais. Essa ambiguidade pode indicar um período

extensional precedendo um evento final de compressão, possivelmente registrado no chamado “Terreno Oriental”, a 530-510 Ma, como discutido em Heilbron et al (2008).

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PARTE IV - ANEXOS: MANUSCRITOS CIENTÍFICOS

ANEXO A

An examination of selected granitoids occurrences in the São Paulo - Ribeira Belt: trace element abundances in zircon as petrogenetic indicators. ANDRADE, S.; ULBRICH, H.H.G.J.; JANASI, V.A.

ANEXO B

Methodology for the determination of trace and minor elements in minerals and fused rock glasses with Laser Ablation associated with Quadrupole Inductively Coupled Plasma Mass Spectrometry (LA-Q-ICPMS). ANDRADE, S.; ULBRICH, H.H., GOMES, C.B., MARTINS, L. **American Journal of Analytical Chemistry**, v.5, p. 701-721, 2014.

ANEXO C

Timing and sources of granite magmatism in the Ribeira Belt, SE Brazil: insights from zircon in situ U-Pb dating and Hf isotope geochemistry in granites from the São Roque Domain. JANASI, V.A.; ANDRADE, S.; VASCONCELLOS, A.C.B.C.; ULBRICH, H.H.G.J.; HENRIQUE-PINTO, R. **Journal of South American Earth Science**, in Press, Corrected Proof on line 24/11/2015 (<http://www.sciencedirect.com/science/article/pii/S0895981115300894>).

ANEXO A

An examination of selected granitoid occurrences in the São Paulo Ribeira Belt: trace element abundances in zircon as petrogenetic indicators

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ABSTRACT

Mass spectrometry with inductively coupled plasma associated with laser ablation (LA-ICPMS) is a powerful tool that allows analytical determinations of trace elements, with high sensitivity and resolution, in zircon and other accessory minerals. This study is a contribution to the knowledge of zircon compositions derived from granitic rocks belonging to the Brasiliano cycle of granite magma genesis in the basement areas of São Paulo state (conveniently divided into “domains”), in southeastern Brazil. Sampled granites in the São Roque Domain are the São Roque, Cantareira and Itaquí batholiths, the Perus and Taipas granites and the Tico-Tico intrusion. The Itu batholith and the Terra Nova intrusion are found in the Jundiá Domain, while the Itaquera samples outcrop in the Embu Domain. Samples from the Ubatuba charnockite and the Ilha Anchieta site belong to the Coastal (Costeiro) Domain.

A preliminary discussion on the contrasted geochemical characteristics is offered for the entire set of samples, identifying chemical parameters that help to define the different granite lineages (e.g., peraluminous or peralkaline character, identification of “I”, “S” or “A” types of granitoids, etc.). Zircons extracted from these granite samples present usually elevated contents of REE, Th and U, with positive Ce and sometimes negative Eu anomalies (Tico-Tico, Itu, Terra Nova, Itaquera, Ilha Anchieta, Ubatuba charnockite and Perus tourmaline granite). High abundances of REE+Y in the analyzed zircons could be created by coupled reactions that occur during zircon crystallization, with substitutions of Si^{4+} by P^{5+} and of Zr^{4+} by REE^{3+} , with charge balance obtained by introduction of Al^{3+} , Fe^{3+} , Mg^{2+} , Fe^{2+} in zircon interstitial sites, controlled by reaction such as $(\text{Y,REE})^{3+} + \text{P}^{5+} = \text{Zr}^{4+} + \text{Si}^{5+}$ (in a 1:1 proportion of REE to P, and similar reactions with proportions 2:1, 3:1 and 4:1). U/Th ratios in general are close to 0.5, expected for zircons of magmatic origin, some grains however presenting values close to 0.1, attesting to a decrease in Th contents probably generated by co-crystallization of the mineral with monazite. Comparison of U/Yb ratios with Hf contents show that the analyzed zircons were generated in a crustal-continental environment. The model Ti-in-zircon geothermometer, determined in zircons with typical magmatic growth textures (e.g., oscillatory zoning overgrowth on idiomorphic cores) yielded reasonable crystallization temperature estimates in comparison with the ones estimated with the zircon and apatite saturation model temperatures in magmas.

Zircons presenting unusual textures (e.g., cores with irregular margins, identifying possible resorption of relicts, or very dark colors under

cathodoluminescence) led to unrealistic temperature estimates of over 1000°C. Positive correlations in Ti versus REE diagrams indicate that an increase in Ti in zircons and, consequently, an increase in their model temperatures of crystallization, can actually be associated with significant substitutions, in zircons, of Zr by Ti, as well as by Si. The same zircon grains also show a remarkable increase in contents of Nb, Ta and P, with positive correlation when compared with (REE + Y) contents, suggesting that these increases in the abundances of those elements (including also Ti) can be a sign of hydrothermal fluid activity during zircon (re)-crystallizations, fluids that are possibly also enriched in halides, alkalies, silica and CO₂. Fluid activity during granite magma crystallization may have been channeled through existing favorable structures, such as the shear zones ubiquitously present in the Ribeira Belt.

Key Words: LA-ICPMS, zircon chemistry, trace elements in zircons, petrogenetic indicators, hydrothermal fluids, Brasiliano granites.

1. INTRODUCTION

Zircon is ubiquitously present as an accessory mineral especially in granitoids, as well as in mantle rocks, meteorites and lunar samples (e.g., Page et al. 2007; Liu et al. 2010). It has been shown that this mineral preserves in its structure and composition a remarkable memory of previous developments, including its first crystallization, as well as ulterior crystallizations, present as external growth zones, with trace elements occupying the sites of Si and Zr in the zircon crystal, the input in its structure tightly controlled by environmental variables, such as ion activities, temperatures, and pressures. Another important characteristic of this mineral is its strong resilience at high temperatures and pressures, typically observed in processes of metamorphism, avoiding an elemental and isotopic diffusive rebalancing in those conditions (Watson, 1996; Watson and Cherniak, 1997).

Zircon, even being an accessory phase, strongly controls the distribution of many trace elements especially in granitic rocks, since it is by structural design and chemistry the natural holder of various trace elements, which have a tendency to exchange place with Si and/or Zr (Belousova et al. 2002), especially when crystallizing from magmas (e.g., Murali et al. 1983). Studies centered on zircon chemistry provide clues about the composition and nature of original parental magmas (e.g., Robatto 2002) and source protoliths and crystallization environment (e.g. Nardi et al. 2012, Trail et al. 2012), as well as indicating genetic granite types (whether type I, S, or A), also pinpointing solidification temperatures, in particular with the use of the recently proposed Ti-in-zircon geothermometry (Watson & Harrison 2005; Harrison et al. 2007).

In granitoid rocks, REE abundances, mostly incorporated into accessory minerals (foremost in zircon, titanite, allanite, and xenotime), diminish with progressive differentiation, as clearly observed in compositions of granitic magmas in these series, without however generating a significant change in the pattern of REE distribution, from the parental liquids up to the more evolved granitic magmas.

The possibility to study the presence and abundance of REE and other trace elements especially in accessory minerals can be performed today with the use of Laser Ablation (LA) techniques applied to single crystals separated from their host

rock. Our study selected zircons contained in several Brasiliano granitoids occurrences, representing various types occurring in the basement areas of São Paulo state, to obtain data on trace element incorporation, to provide new interpretations relying heavily on considerations that this new chemical technique can bring to this subject.

The basement areas of the state of São Paulo, southeastern Brazil, is mostly made up by a large variety of metamorphic rocks, ranging from low-grade metamorphic facies (e.g., São Roque group of rocks) to terrains where high-grade types are predominant (e.g., Ubatuba charnockites). A remarkable feature of this basement region is the presence of large amounts of granitoids occurrences, mostly referred to the activity of the so-called Brasiliano cycle of tectonics, metamorphism, and magmatism. These granitoids were grouped in earlier studies mostly according to their shape and/or deformation pattern, as: 1) pre-orogenic types, mostly represented by strongly deformed bodies; 2) syn-orogenic ones recognized by their elongated shape with a NE-SW direction, the predominant structural trend in SE Brazil, and 3) late- to post-orogenic massifs, mostly represented by undeformed bodies with a tendency to form broadly equidimensional to rounded outcrops patterns. More recent studies, performed in the 80's and 90's, clarified aspects by mapping in detail many of these bodies, adding data to show the extreme complexity of most of them (e.g., batholiths such as Cantareira, São Roque, Itu, Itaquí and Morungaba), as well as smaller bodies such as the ones outcropping in Piedade, Piracaia and Perus (Taipas, Tico-Tico, etc.).

The method of study adopted in this paper, given the extraordinary complexity of the granite geology in the state of São Paulo, was to select some rather distinct samples representing many granitic bodies, also based on the knowledge gained in the last decades about these rocks in our state. Thus, an admittedly biased group of samples was selected, a bias that can be explained because the knowledge about the respective granitic bodies, as well as about the regional context, was vastly increased in the last few years, on account of research activities heavily relying on chemical and isotopic determinations with a modern bias. Whenever possible, given the poor outcrop pattern that is the common rule in São Paulo state, fresh and large

samples were obtained from quarries and larger road cuts, later used in chemical studies and providing the materials for extraction of zircon single crystals.

2. GEOLOGICAL FRAMEWORK

The basement area outcropping in the state of São Paulo comprises two different types of rocks, one being the country rocks developed through complex phenomena during geologic history, beginning with sedimentation and following with a protracted sequence of deformation and metamorphism, constituting several still incompletely defined basement “complexes”, in part also invaded by older (pre-Brasiliano) granites, now heavily deformed, in turn cut by a bewildering variety of later granitic magmas, occupying about 30% of the exposed basement areas. This late granitic plutonic activity, generally referred to as the “Brasiliano event”, lasted from about 600 Ma to about 480-450 Ma, encompassing all types of granitic plutons, some clearly early- or syn-tectonic occurrences usually defined by their elongated oriented form, and also others that are clearly representing late tectonic or even post-tectonic occurrences.

A very prominent feature in this basement region, as in the entire section covering southeastern and southern Brazil, is the presence of shear zones of regional extent, all bearing a predominant NE-SW direction, therefore providing the possibility to divide these basement areas into several “domains”. Such a domain map for the state of São Paulo is presented in Figure 1 (source: Janasi & Ulbrich, 1992;), showing the positions of the numerous granitic occurrences conveniently divided up into pre-tectonic occurrences (deformed, mainly converted into gneisses), “dry” granitoids (charnockites and mangerites), syn- to late tectonic bodies (the predominant type, including nebulitic occurrences as well as porphyritic to equigranular granites of several ancestries, referred to as “I” and “S” type granitoids) and post-tectonic (“post-orogenic”) varieties (for a more recent outline of the “domain” structure of the basement areas in SE Brazil, cf. Janasi et al., 2015, and bibliography cited therein). The noteworthy NE-SW structural trend observed in Figure 1, very marked in S-SE Brazil and controlled by the direction followed by the predominant regional shear fracture zones and notably represented by the arrangement and form

of several granitic bodies, allows also to propose for this basement region a “domain” structure with limits between the different basement units given by the most prominent shear zones. The recognized domains (in Janasi & Ulbrich 1992; cf. also Janasi et al., 2015), which mostly continue into the neighboring states of Paraná (to the south and southwest) and Rio de Janeiro and Minas Gerais (to the north and northeast), are named as follow: the Iguape and Ubatuba domains (coastal units), Açungui and Embu domains (projecting into Parana state, the last one farther north into Rio de Janeiro), the thin slice of the São Roque domain, and also the Amparo, Jundiáí and Guaxupé units. The western limits are given by the outcrops of the Paraná basin strata covering basement rocks (Figure 1).

The granitic bodies sampled in our study are indicated in Figure 1. In the *São Roque domain*, the selected massifs were the Itaquí, São Roque and Cantareira batholiths, the Taipás stocks and the Tico-Tico intrusion, as well as a stock belonging to the group of the Perus tourmaline granites. The Itu batholith and the Terra Nova intrusion are located within the *Jundiáí domain*, while the Itaquera outcrops, positioned within the *Embu domain*, are now virtually inaccessible because of their location in the eastern boroughs of the capital city of São Paulo. The Ubatuba occurrences of “dry” granitic types are located within the *Ubatuba domain*, together with the Ilha Anchieta sample, the last one an island occurrence.

A more detailed map of part of the São Roque domain is shown in Figure 2, indicating the positions of the Cantareira and Itaquí batholiths, as well as those of the three Taipás stocks and the Tico-Tico intrusion, and also the area in which the several bodies of the Perus tourmaline granites are found (compilation map by Azevedo, 1997).

Figure 1. Simplified map of the granitic occurrences observed in the basement areas of São Paulo state, southeastern Brazil. Large-scale shear zones with a general NE-SW trend, the prevalent structures in this area, are also the limits of several basement domains, as indicated (respectively, domains Guaxupé, Jundiaí, Amparo, São Roque, Embu, Açungui, Iguape and Ubatutba; cf. text). Studied units are identified as follows: *São Roque domain*, C: Cantareira; It: Itaquí; SR: São Roque; Ti: Tico-Tico; *Jundiaí domain*, Itú; TN: Terra Nova; *Embu domain*, Itaq: Itaquera; *Ubatuba domain*, Cha: Ubatuba charnockite; IA: Ilha Anchieta. For other occurrences, see locations in Figure 2. Source: Janasi & Ulbrich, 1992.

Figure 2. Map of part of the São Roque domain (as defined in Figure 1), indicating the complex relationship between structure of the basement rocks and the emplacement of some of the studied São Roque granitoids. 1: Cantareira; 2: Taipas; 3: Perus; 4: Tico-Tico; 5: Itaqui. Some other granites appear as smaller, elongated, mostly E-W trending strips, belonging in part to pre-Braziliano deformed granitoids intrusions; the granite body to the N of Cantareira is the Mairiporã Granite. Source: Azevedo, 1997.

3. THE SAMPLED GRANITOID OCCURRENCES

A brief description of the several sampled granitic occurrences is given here, as a reference framework to show the complexities found in the several Brasileiro granite intrusions (for previous references, see Janasi & Ulbrich, 1992; also Azevedo 1997 and Janasi et al. 2015, for additional bibliography and a summary of geological features).

3a. Occurrences in the São Roque Domain

The granites sampled in the São Roque domain (as defined in Janasi & Ulbrich, 1992; Figure 1) come from the following occurrences: Cantareira batholith, Taipas stocks, Perus tourmaline granitoids, Itaqui and São Roque batholiths, the Tico-Tico intrusion.

Cantareira batholith

This intrusion, studied mainly by Dantas (1990), is one of the largest granitic bodies exposed in the state of São Paulo, covering about 320 km². It is broadly elongated along the regionally predominant NE-SW direction. Contacts are mainly tectonic, limited mostly by the Caieiras (northern part) and Mandaqui (western limit) shear zones. Nine predominant facial types were recognized in the batholith. The *Pirituba facies* (cream-colored massive porphyroid type), the *Canivete unit* (bluish grey porphyroid facies) and the *Itaguassu type* (porphyroid rosy facies) are mostly biotite granodiorites and monzogranites, predominant in the central and SE part of the massif (Pirituba) and to the SW (Canivete) and scattered within the entire massif as irregular masses (Itaguassu), presenting mostly non-oriented K-feldspar megacrysts and biotite, with little hornblende, as main mafic phase ; all show several types of enclaves. The *Mandaqui type* (orthognaissic facies), porphyroid granodioritic to monzogranitic in composition, shows rounded megacrysts of K-feldspar set in a groundmass with mylonitic to blastomylonitic texture, restricted to locations along outer contacts and along fault zones cutting the batholith. The *Tremembé type* (grey equigranular facies) appears as grey monzogranite concentrations with enclaves in dykes and irregular smaller bodies distributed all along the batholith. The *Petrópolis type* (pegmatoid facies) constitutes smaller irregular masses of granodiorites to

monzogranites, with plenty of K-feldspar phenocrysts and presence of microgranular and micaceous enclaves. The *Hortolândia* type (grey inequigranular facies) shows inequigranular monzogranites to granodiorites, with an oriented texture and presence of enclaves, found along the NE contact zone, grading into porphyroid facies. The *Santa Inês* type (migmatitic or banded facies) is made up of porphyroid granodiorites with plenty of biotite and an oriented (flow?) structure, found mainly along the N border. The *Jaraguá* type (leucocratic equigranular facies) is present as irregular concentrations and dikes of leuco-quartz monzonites, sometimes appearing with a marked hydrothermal alteration. Dantas (1990) positions the entire magmatic activity as synchronous to the D2 deformation phase observed in the metamorphic country rocks (São Roque Complex s.l.). Wernick et al. (1993) recognize four distinct magmatic pulses as the cause for the emplacement of the batholith.

Taipas stocks

Azevedo (1997) found that the Taipas massif, formerly mapped as a larger stock, has to be divided into three separate intrusions, petrographically very similar to each other and to the Pirituba facies in the Cantareira body. These stocks are located close to the southwestern border of Cantareira (Figure 2). Porphyritic textures (with K-feldspar megacrysts) are predominant in these monzogranites (to granodiorites and tonalites).

Perus tourmaline granitoids

Outcropping in an area immediately to the west of the Cantareira massif, these rocks appear as dikes and some small stocks, not larger in dimension than 100 to 200 m, sustaining quarrying activities in the immediate past. The rocks have as a common feature the presence of tourmaline, as well as the complete absence of biotite. These occurrences caught the attention of geologist and mineralogists in the past on account of the presence of tourmaline, as well as of other rare minerals (cf. Azevedo, 1997, for a bibliography on this subject). The occurrences were mapped and studied more recently in detail by Azevedo (1997), who recognized several facies types. The one which is predominant in the stocks is a remarkable *layered facies*. Each layer, with a thickness not surpassing a few cm, appears in association with other similar layers, thus repeating structures such as the ones observed in the

remarkable basaltic stratiform intrusions. The layers appear deformed and folded, possibly on account of a syn-magmatic deformation generated by the still active shear zones on the layered sequences present as a crystallizing magmatic mush (cf. Azevedo, 1997, and discussion therein). The most common structure is the one where each layer shows a rapid gradation between the lower and middle parts, presenting variations in the contents of feldspars and quartz, and lesser amounts of tourmaline, which usually concentrates in the upper level; other distributions were also found, such as the one where tourmaline concentrates in the lower level, a much rarer case. A non-layered *homogenous facies*, also described, is much rarer. A *pegmatitic facies* is also present, especially in the stocks, where this type can occupy as much as 20 to 40% of the quarried central areas (the *internal pegmatitic facies* of Azevedo, 1997). Many of the dikes outcropping in the same region are entirely made up of tourmaline pegmatites, genetically related with the layered granites (the *external pegmatitic facies* of Azevedo 1997).

Itaqui batholith

This multiple intrusion was mapped in detail by Ferreira (1991, 1997). It shows a broadly triangular form, covering around 120 km², cut in its southern part by the Taxaquara shear zone. The first intrusions are those of the porphyroid granodioritic *Barueri* and the monzogranitic *Pedreira Cantareira* unit, both with biotite and hornblende. The following intrusions are the dikes of the *Torre* equigranular biotite monzogranite and the *Cruz Preta* porphyroid biotite quartz monzonite. A third phase of intrusions is represented by the biotite monzogranites of the *Aldeia da Serra* and *Mutinga* stocks, respectively positioned at the southwestern and southeastern part of the batholith. A last intrusive phase is represented by the dikes of the *Suru* monzogranites and some tourmaline aplites.

São Roque batholith

This batholith, broadly triangular in shape and covering a surface of roughly 160 km², was mapped in detail by Coutinho (1953) and later by Andrade (1993). Contacts are tectonic, to the south, at the base of the triangle, with the Taxaquara fault, to the west with the Mairinque fault along 38 km, and to the east, showing an arcuate shape with the Araçariquama shear zone. It is, both petrographically and

structurally, similar to the Itaquí batholith, however presenting small pockets of intrusions of tourmaline granites, absent in the Itaquí body (Andrade 1993; Wernick et al. 1995a). Clusters of pegmatitic smaller bodies are commonly distributed both through the more equigranular as well as in the porphyroid facies, constituted mainly by euhedral to subhedral K-feldspar crystals.

Tico-Tico intrusion

This intrusion, studied earlier by Moraes Rego (1933) and renamed Anhanguera in a later study by Penalva & Hasui (1970), is an elongated body covering about 11 km², with a general east-west orientation. The main components are inequigranular syeno- to monzogranites, with biotite and magmatic muscovite, garnet, some tourmaline and plenty of zircon; structure is generally massive, sometimes also showing a weak planar orientation. Deformed pegmatitic veins and dikes with a granitic composition are also found, presenting tourmaline concentrations in its central part, accompanied by muscovite crystallization along the contact with the metamorphic country rocks. It is classified as a late-tectonic granitoid.

3b. Occurrences in the Jundiaí Domain.

The Itu batholith and the Terra Nova intrusions are both positioned within the Jundiaí domain (Figure 1), which forms a part of the so-called Median Guaxupé Massif, constituted by quartzites, schists and gneisses (frequently migmatitic), pertaining possibly entirely to the tectono-metamorphic pre-Brasiliano Piracaia complex (Campos Neto et al. 1983).

Itu batholith

It is the largest granitic body mapped in the Jundiaí domain, covering around 390 km², of which over 200 km² can be easily visualized, mainly appearing as large boulder fields and horizontal flat-lying exposures. It is formed mainly by the three separate intrusions named Salto, Cabreúva and Indaiatuba that, in part, present texturally features reminiscent of rapakivi facies (e.g., large sub-rounded to sub-

idiomorphic K-feldspars megacrysts, sometimes also showing plagioclase mantling a core feldspar) and of other, less characteristic type-A calc-alkaline intrusions, such as the Itupeva body. Both equigranular as well as porphyritic biotite syenogranites are the predominant varieties in the rapakivi facies, all of them showing abundant accessory zircon (see Galembeck 1991, Galembeck et al. 1991, Wernick et al. 1995b).

Terra Nova intrusion

It is found within the Jundiaí domain (Figure 1), which forms a part of the so-called Median Guaxupé Massif, constituted by quartzites, schists and gneisses (frequently migmatitic), pertaining possibly entirely to the tectono-metamorphic pre-Brasiliano Piracaia Complex (Campos Neto et al. 1983). The granitic massif itself covers about 23 km², presenting an irregular form, partly elongated in a NE direction. It is constituted mainly by rosy-colored equigranular biotite granites, which may show locally along its borders an oriented grey granite (Hasui et al., 1978). Biotite is the predominant mafic mineral, with sodic amphibole in the rosy facies, while common hornblende is present in the grey granite.

3c. Occurrences in the Embu Domain

The central part of the Embu Domain is almost entirely covered by the city of São Paulo and surrounding areas, and the definitions of the described granite occurrences rely heavily on earlier work.

Itaquera intrusion

Although now almost completely destroyed and covered by urban development, a few inactive former quarries can still be sampled, showing some good examples of this rock, known commercially as the “Itaquera granite”, borrowing its name from the geographic locality, in the last years made famous as the name of the stadium which is host to one of the most popular football teams in São Paulo. The granite is a two-mica, mainly equigranular facies, which according to one earlier report forms a rectangular body, 14 x 3 km, about 40 km² in size (represented as such in IPT 1981, the official map of the state of São Paulo), while other authors

restrict its size to no more than 2 km², supposedly presenting gradations towards tonalitic gneisses with garnet and muscovite (see Janasi & Ulbrich, 1992).

3d. Occurrences in the Ubatuba Domain

The Neoproterozoic Ribeira Belt in SE Brazil is represented by different geologic domains in SE São Paulo, developed around the SE border of the São Francisco craton, as a consequence of convergence with another plate positioned to the East (Brito Neves et al., 1999; Heilbron & Machado 2003). The Rio Negro magmatic arc was formed at that time and accreted against the São Francisco continent by means of a frontal collision around 590 to 550 Ma ago. Two main geologic domains can be distinguished in the Ribeira belt in São Paulo, the first one known as the Embu domain (mainly formed by supracrustal metamorphic rocks with a medium grade, deformed and metamorphosed around 800 Ma ago, followed by several granite intrusions, of which one dated around 600 to 580 Ma is the more remarkable (Janasi et al. 2003). The other unit is the Coastal (Ubatuba) domain, made up of granitic and orthogneissic rocks, with some higher grade migmatites. Rocks of the Ubatuba domain are relatively younger than the ones in the Embu domain, presenting Sm-Nd ages of less than 1.5 Ga, in comparison to Sm-Nd ages of 2.0 Ga detected in the Embu domain. The igneous rocks in the Coastal (Ubatuba) domain show a higher-grade metamorphism, evolved around 590 Ma, an age that coincides with the ones determined for some syn-orogenic correlated granitoids (e.g., the Natividade da Serra elongated batholith presenting two-mica granites; Janasi et al., 2003).

Ubatuba granitoids

These granitoids, petrographically quartz mangerites to charnockites, are observed in association with some local dioritic bodies; they are usually deformed and present a secondary foliation, but may also be found as non-deformed intrusions, as observed in several poorly-known occurrences, such as the Guarujá Granite (Dias Neto et al. 2008) and the Santos body (Silva et al. 2005). They are mostly inequigranular, medium- to coarse-grained, characterized by greenish-grey colors.

Associated leucogranites are similar in texture and deformation, but are rosy to reddish in color, with minor amounts of mafic minerals (CI around 4-5).

Ilha Anchieta granitoids

These rocks outcrop on an inland with a general triangular form, mainly occupied by several granitoids facies (Janasi & Ulbrich, 1992). To the NE and NW, augengneisses are observed, while charnockites and leucogranites appear as a N-S trending strip, 2 km wide, in the western part of the island. Quartz monzonites are also observed in other areas.

4. PETROGRAPHY OF THE GRANITOID ROCKS

4a. São Roque domain: Cantareira, Taipas, Perus, Tico-Tico, Itaqui, São Roque

Cantareira and Taipas. One Cantareira rock (***Cant-6***, porphyritic biotite monzogranite representing the Pirituba facies (Figure 3a), cf. Dantas, 1990) was collected within the Basalto quarry (Av. Raimundo Pereira de Magalhães, 2547 - close to the Mario Covas “Rodoanel”; cf. Figure 2). A second Cantareira sample, ***MD-42B***, comes from a satellite body from a highway cut at the Bandeirantes Highway (close to km 26), representing an inequigranular syenogranite of the Canivete facies of Dantas (1990). Sample Cant-6 (Figure 3b) presents a porphyritic texture, with large microcline grains with Carlsbad twinning associated with plagioclase and surrounded by quartz; CI is around 10 to 20. K-feldspar is almost without perthites, somewhat altered to sericite, with idiomorphic to irregular inclusions of altered plagioclase, with reaction rims, as well as inclusions of biotite and opaque minerals. The plagioclase is altered (to sericite), also showing titanite and epidote. Quartz is deformed and shows mosaic structure and undulatory extinction. Mafics are distributed in a uniform manner. Biotite, mostly deformed, and amphibole are greenish-brown. The main accessory minerals are zircon, titanite, apatite, and opaques (magnetite).

Figure 3: (a) Cantareira sample Cant-6 collected at the Basalto quarry. (b) Thin section image of Cant-6 showing albite twins in altered plagioclase, Carlsbad twinning in K-feldspar, and quartz mosaics, plus mafic aggregates (mainly, biotite and opaques).

The rocks from the Taipas stock (**TAP-1**, main porphyritic biotite monzogranite) and a corresponding hololeucocratic dike rock (**TAD-1**) were taken from the Construcap-Agis quarry (Figure 2). Figure 4a shows the main Taipas porphyritic facies cut by the hololeucocratic dike, the last one showing irregular boundaries, suggesting that the dike represents a generation by lateral diffusion and collection of residual magmatic liquid into dilatational fractures; these dike granites should therefore represent the most fractionated liquids formed during the crystallization of the main porphyritic facies.

Figure 4b presents a thin section image of the Taipas *main granite*, with clear indications of deformation and some recrystallizations of magmatic textures. This granite has a color index of around 15 to 20, with tabular plagioclase slightly altered to sericite, fresh K-feldspar both as megacrysts (cm-sized) and in the groundmass, showing small amounts of localized fine string perthites; cross-twinning is poorly developed. Quartz is frequently observed as mosaics with irregular grain boundaries, usually with undulatory extinction. Non-oriented mafic aggregates are irregularly distributed in the rock, always showing smaller grain size as the felsic phases, mostly constituted by anhedral brown-greenish to yellowish biotite (sometimes presenting deformation by bending), accompanied by irregular to euhedral titanite, zircons (as small inclusions, often with pleochroic haloes), as well as some allanite and tourmaline, and opaque minerals (mostly magnetite, ilmenite and sulfides); dark-greenish pleochroic amphibole with irregular outlines is relatively rare.

The *dike granite* also shows a tendency to a porphyritic texture, with large K-feldspars (with irregular outlines, partly perthitic, cross-twinning observed but not very frequent), in a groundmass with tabular to irregular plagioclase, with fine albite twinning, frequently deformed, also associated with smaller-grained K-feldspars. Plagioclase usually shows sericite appearing along twinning surfaces, the sericite (with some clinozoisite) also cutting as veins the fabric of the rock. Quartz is present as mosaics, with irregular outlines and undulatory extinction, and as smaller veins and elongated mosaics cutting the fabric of the rock. Some small aggregates present chlorite, biotite, and titanite, with opaque minerals and epidote-clinozoisite (as plagioclase alteration) also visible; titanite is frequently idiomorphic, somewhat rounded, and zircon, as inclusions in biotite, may grow up to 0.3 mm.

Figure 4. **a)** The Taipas porphyritic monzogranite shows K-feldspar phenocrysts. Hololeucocratic (dilatational) dike cuts the main rock with slightly irregular borders, almost devoid of mafic phases. See comments in text. **b)** Thin section (TAP-1a) photograph of the Taipas granite, presenting slightly altered plagioclase (to sericite), with K-feldspars and quartz with irregular outlines, present as mosaics (especially quartz); biotite, titanite and magnetite form finer-grained aggregates.

Perus tourmaline granite. One of the samples of the Perus tourmaline granites is **Pe-04**, taken from a road cut (most of the formerly active quarries are now destroyed by road construction of the Mário Covas “Rodoanel” SP-21). When occurring as stocks, it is a mostly equigranular tourmaline granite with a marked layered structure, each layer with a thickness of a few cm, always presenting tourmaline as mafic mineral (Figure 5a). Predominant minerals are microcline, unzoned sodic plagioclase and quartz with clear signs of pos-magmatic deformation (Figure 5b). Tourmaline, faintly zoned, is always prismatic-idiomorphic, variable in

sizes, also showing, infrequently, clear indication of brittle deformation (e.g., appearing as broken crystals and with transversal fractures); pleochroism is from olive-green to pale yellowish. Plagioclase is tabular-sub idiomorphic, with sizes up to 3 mm, with irregular outlines, presenting albitic outer borders and fine albite twinning, sometimes with curved (deformed) surfaces; alteration to sericite is faint. Accessory minerals are some apatite, also idiomorphic magmatic garnets and zircon (sometimes rounded, appearing rarely: a relictic phase?).

Figure 5. **a)** Layered and deformed structure in the Perus tourmaline granites. Layers are marked by the heterogeneous distribution of tourmalines, concentrating generally in the upper part of the layers; they can repeat themselves several dozen times, always showing clear signs of deformation (folding). **b)** Thin section (Pe-3) image of the Perus tourmaline granite (Pe-4a). Texture is equigranular to inequigranular, with tabular to irregular feldspars and mosaics of quartz, showing also tendency of concentration in the distribution of the always idiomorphic-prismatic tourmaline grains.

Tico-Tico granite. This rock, mostly a two-mica garnet-bearing somewhat porphyritic leucogranite, is represented by samples **Tico-1** and **Tico-2** (taken from the Pedrix quarry, located along the Bandeirantes Highway, km 30). It shows as larger grains K-feldspar, plagioclase with a tabular habit, quartz mosaics and biotite, accompanied by primary larger plates of muscovite, some tourmaline, zircon and idiomorphic magmatic garnet (Figure 6a, 6b).

Figure 6. **a)** Hand specimen of the Tico-Tico granite, showing a massive inequigranular structure. **b)** Thin section (Tico-2a) of the Tico-Tico rock, with inequigranular texture, perthitic K-feldspar (string perthites) with somewhat altered plagioclase and mica inclusions, quartz mosaics, and mafic aggregates (biotite predominant); muscovite is present usually as finer-grained lamellae.

Itaqui granite. The Itaqui granite shows a large variety of rock types, of which a few were sampled for our study, at the quarry administered by the Polimix construction company (location between Santana do Parnaíba and Barueri, outskirts of São Paulo); here, Barueri is the predominant facies (Ferreira 1991, 1997), an inequigranular to porphyritic granite, with variable amounts of megacrysts (samples **ITQ-2**, **ITQ-4**; Figures 7a, 7b), at the same time also exhibiting several types of dike rocks (Figure 8a, 8b) and plenty of microgranular enclaves (Figures 9a, 9b). Another sample (**MD-24**), a porphyritic hornblende-biotite monzogranite, was collected along the Fazenda Itahyê road, taken from a minor satellite stock that probably is a marginal body related with the main Itaqui granite.

Figure 7. **a)** Itaqui granite, mostly equigranular facies. **b)** Itaqui granite, massive porphyritic facies (with cm-sized K-feldspars).

Figure 8. **a)** Main Itaqui granite, showing variations in megacryst contents, cut by two subhorizontal hololeucocratic dikes with irregular borders (compare with Figure 4a showing a dike in the Taipás occurrence). **b)** Hand specimen of a dike rock in the Itaqui quarry.

Figure 9. **a)** Outcrop surface showing microgranular enclaves with typically rounded shapes, in a leucocratic portion of the Itaqui granite ("mingled" structure). **b)** Hand specimen of a microgranular mafic enclave in the Itaqui quarry, carrying (mingled?) feldspar megacrysts.

The *dyke rocks* at Itaqui are hololeucocratic, with slightly altered plagioclase (into sericite), microcline and quartz mosaics, and muscovite appearing as bands and veins, sometimes also as large milimetric blades as depicted in Figure 10 (magmatic muscovite?).

Microgranular enclaves (monzonite to quartz monzonite) present more equigranular and finer-grained textures, with a predominant network of mafic aggregates (with green to yellowish amphibole (with opaque inclusions) as principal mineral, together with subordinate greenish-brown to yellowish biotite, and idiomorphic titanite, pale-yellow monazite and zircon), separating mosaics with both

feldspars associated with subordinate quartz; plagioclase presents here fine regular Albite twinning, with plenty of sericite (sometimes also epidote) as separate platelets, while cross-twinned K-feldspar, relatively unaltered and with little or no perthites, shows inclusions of amphibole.

Figure 10. **a)** Thin section of the dyke rock at Itaqui, showing plagioclase, quartz, biotites and magmatic muscovite. **b)** Thin section (ITQ-2.1) with inequigranular texture of porphyritic facies; Feldspar groups (plagioclase somewhat altered, cross-twinned K-feldspar with irregular outlines) amidst quartz irregular crystals and irregular mafic biotite-amphibole aggregates.

In the Polimix quarry, *sheared very thin rock slices* are frequently observed, indicating a rather marked post-magmatic activity of the regional stress fields, where the granite minerals were sheared and substituted by a greenschist type of alteration mineralogy (amphibole, epidote, quartz mosaics and titanite).

São Roque granite. A representative sample of the São Roque granites was collected along a road cut on the Livio Tagliassachi Road, close to its junction with the Castelo Branco highway (sample **SR-07**). It is in general similar petrographically to the main porphyritic granites found in the Itaqui intrusion (Wernick et al. 1995a), representing a porphyritic hornblende-biotite monzogranite, showing plenty of accessory titanite and zircon, as well as also rounded aggregates with idiomorphic tourmaline, a mineral that in the Itaqui body was found only in some late aplites (Ferreira 1991; Ferreira & Wernick 1991).

4b. Granites in the Jundiá domain: Terra Nova and Itu.

Two granitic bodies were sampled in the Jundiá domain, the minor Terra Nova intrusion and some samples from the large Itu batholith.

Terra Nova. A sample (**TN-1**), from the Terra Nova intrusion was collected at the Terra Nova quarry (Tavares Pinheiro Company; km. 49 of the Anhanguera Highway). It is a reddish porphyritic granitoid (Figure 11a), with subidiomorphic to irregular feldspars; one, a perthitic K-feldspar presenting perthites and cross twinning, the other a finely twinned subhedral to anhedral plagioclase with incipient alteration. Biotite is the main mafic mineral, often altered to chlorite. Muscovite is usually present as minor flakes; rarely, it is observed as larger lamellae. Fluorite, apatite, zircon and opaque grains (magnetite and pyrite) are the main accessory minerals (Figure 11b). Mafic microgranular enclaves, irregularly distributed, are also observed, a feature Terra Nova shares with many Itaqui facies.

Figure 11. **a)** Hand specimen of the Terra Nova granitoid. **b)** Thin section (TN-1b) of the Terra Nova granitoid, showing subidiomorphic plagioclase crystals with bent and broken albite twins, K-feldspar with irregular flame perthites, and quartz as irregular mosaics. Biotite (in aggregates and also as separated crystals) partly altered to chlorite.

Itu granite. The Itu sample (**ITU-14X**) was collected along the Itu-Salto highway SP-071, close to the entrance to the Salto Township (km. 1.5). It is a porphyritic to inequigranular rosy-colored muscovite-biotite monzogranite, showing a slightly oriented fabric (Figure 12a). The larger subidiomorphic-tabular (more than rounded) K-feldspars appear mantled by whitish plagioclase, thus mimicking a rapakivi structure. K-feldspar, the main felsic mineral, is subhedral and slightly zoned:

margins are homogeneous, with little alteration, while cores present a powdery fine-grained alteration (kaolinite?). Sometimes, string perthites are observed. Plagioclase is also present as megacrysts, subhedral to anhedral, with numerous fine twinning and incipient alteration (which, when concentrated along twin individuals, appears with a brownish color). The groundmass presents the same minerals, K-feldspars now more irregular and with tiny string perthites; plagioclase is somewhat altered into sericite, zoned, with cores showing higher alteration (Figure 12b).

Figure 12. **a)** Hand specimen of a representative sample of Itu rocks with a rapakivi structure. **b)** Thin section (ITU-14Xa) image of the rapakivi facies of the Itu granitoid. Inequigranular texture has showing K-feldspar with irregular borders, partly perthitic (flame to string perthites). Irregular mafic aggregates show dark brown biotite with plenty of inclusions (especially zircons) together with a second-generation paler biotite almost free of inclusions.

4c. A granite in the Embu domain: Itaquera.

The two collected samples from Itaquera are represented in Figures 13a and 13b (samples **ITA-1** and **ITA-2**). The rock is a two-mica granite, equigranular to inequigranular with feldspars as main minerals. Foliation is present, visible mainly in the orientation of the mafic aggregates. K-feldspar is microcline (cross twinned), with irregular outlines, with little or no alteration. Myrmekites are frequently observed, with rounded outlines projected into the feldspar grains. Plagioclase is tabular, zoned, with fine albite twins, subhedral to anhedral, always with some sericitic and carbonate alteration (also epidote), sometimes localized along twin lamellae. Quartz is present as finer-grained mosaics. The mafic phases, mostly constituted by micas

and accessory minerals (zircons, apatite and opaques), are almost always present as oriented aggregates. The usually fresh biotite (alteration to chlorite is observed) has a peculiar pleochroism, from reddish-brown (“foxy-red”) to faint beige colors, with abundant zircon inclusions, mostly showing pleochroic haloes; cleavages may be bent in some cases; the mineral may also appear as isolated plates dispersed through the thin section. Primary muscovite appears in subordinate amounts, with sizes comparable to those of biotites. Titanite seems to be absent in these granites. The rock was clearly deformed, subject to some degree of hydrothermal alteration and then recrystallization. Thin sections are represented in Figure 14a and 14b.

Figure 13. **a)** A sample of inequigranular Itaquera granite (ITA-1), with predominant K-feldspar grain and whitish plagioclase. Mafic aggregates, partly oriented, present mainly the two micas as constituents. **b)** A more equigranular Itaquera granite (sample ITA-2) with a finer-grained more leucocratic dike cutting the main granite.

Figure 14. **a)** Thin-section (ITA-1a) image of the Itaquera rock with square to more elongated irregular feldspar mosaics (K-feldspar shows cross-twinning; plagioclase is slightly altered and conspicuously zoned; quartz is present as irregular to elongated mosaics). Biotite, with some muscovite, is oriented along possible fractures within the rock. **b)** Thin section (ITA-1b)

of a somewhat inequigranular Itaquera sample with subhedral and zoned, slightly altered plagioclase, cross-twinned K-feldspars and quartz mosaics, with biotite and associated muscovite, partly oriented (along fractures?); pleochroic haloes visible in biotites.

4d. “Dry” granites in the Ubatuba domain: Ubatuba, Ilha Anchieta.

Two samples of granitoids, one of them a representative of a “dry” facies (a charnockite), were collected in the Ubatuba domain.

Ubatuba charnockite. The sample (**CHA-1**) was collected in an abandoned quarry named Pedreira Itamambuca, close to the km 36 of the Rio-Santos highway (BR-101), 13 km north of Ubatuba city at the Itamambuca beach. It is a grey-greenish rock, extremely fresh, coarse-grained with mafic cm-sized aggregates; CI is around 10-15 (Figures 15a, 15b). K-feldspar is fresh, homogeneous (no twins) and with only some tiny perthites appearing in sectors of the host grain; optically, it is an orthoclase, frequently presenting plagioclase inclusions. Plagioclase presents very fine twins, no alteration, and also some antiperthites (irregular to square patches). Quartz shows a variety of sizes, appears in mosaics, with undulatory extinction. Accessory minerals are zircon, opaques, apatite; no titanite was observed. The mafic aggregates show mainly brown amphibole with irregular outlines, with pleochroism from dark brown (almost opaque) to yellowish-brown. Pyroxenes are important additions, the clinopyroxene appearing as extremely irregular, mostly elongated grains, with a faint greenish, slightly pleochroic color. Orthopyroxene is intergrown with the monoclinic variety, appearing again as very irregular grains, clear colors, with inclusions (apatite, opaques, and plagioclase). Biotite is subordinate, mostly associated with amphibole, presenting a pleochroism from brownish-orange to very dark brown (Figures 16a, 16b).

Figure 15. **a), b)** Ubatuba charnockite samples showing mafic minerals as very distinct anhedral aggregates. The samples present K-feldspar, two pyroxenes, greenish amphibole and dark brown biotite.

Figure 16. **a)** Thin-section (CHA-1A) image of Ubatuba charnockite (parallel nichols). Somewhat inequigranular texture, with remarkable mafic aggregates (two pyroxenes and a greenish amphibole, with subordinate strongly pleochroic brown biotite) in a groundmass with very fresh orthoclase and plagioclase, together with irregular, smaller quartz grains. **b)** Same image as before with crossed nichols.

Ilha Anchieta. The collected sample (**A-10**) is a porphyritic biotite-hornblende quartz monzonite (CI around 10 to 15; cf. Azevedo Sobrinho et al. 2011)). Tabular to oval-shaped microcline (cross twinning) prevails as megacrysts, also present in the groundmass; it shows some alignment, with perthites appearing powdery as a result of alteration (to clays?). Plagioclase is tabular to anhedral, with some alteration (especially visible sericite), in part also presenting epidote. Myrmekites are observed in contacts of the two feldspars. Quartz, always with irregular to rounded outlines,

presents undulatory extinction. Accessory minerals are zircon, titanite, apatite, allanite and opaques.

5. ANALYTICAL METHODS

A brief description of the several chemical methods used to identify the compositional parameters is here offered. A more detailed treatment can be found in selected papers dealing with the methodological aspects, also cited in the following lines.

5.1. Whole-rock geochemistry: major, minor and trace element determinations

X-ray Fluorescent technique (XRF) is mainly used for the determination of major, minor and some trace elements in rocks. The technique begins with the selection of mainly clean and unaltered samples (typically, several kg), then fragmentation followed by grinding to small grain sizes (less than 200 mesh) that allow easy preparation of pressed pellets and fused-glass samples (cf. details in Mori et al., 1999). The determinations were realized with a Philips spectrometer model PW2400, with a Mo tube and an automatic sampler, at the XRF Laboratory of the recently created NAP-Geoanalítica facility at Instituto de Geociências - USP. Issues related to contamination during preparation of powdered samples are addressed and discussed in detail in Sertek et al. (2015).

5.2. Whole-rock geochemistry: determination of REE and other trace elements with ICP-MS.

The used methodology to determine the abundances of rare earth elements and other trace elements relies on a quadrupole ICP-MS spectrometer at the ICP-MS Laboratory of the Instituto de Geociências - USP, an iCap-Q model of the Thermo-Analytical manufacturer. The procedure begins with about 40 mg of powdered rock sample, dissolved in Parr bombs in an electric oven, with the addition of nitric acid and HF, heated to about 200°C for around 5 days, cooled and then heated on an

electric plate for vapor-separation of Si as SiF₄. Details of the method are described in Navarro et al (2008).

5.3. Zircon chemistry

The methodology used for chemical determinations in zircon is briefly mentioned here.

Separation of zircon from the host rocks. In a summarized way, the steps to be taken are the following: **A)** selection of clean samples of the host rock (ca. 0.5 to 3 kg of acidic rocks, up to 20 kg when the samples are basic rocks), which then are crushed to appropriate sizes in a jaw grinder. **B)** the fraction between 100 and 250-mesh is separated from the crushed material, using sieves. **C)** the obtained fraction is then positioned onto a vibratory table to separate heavy phases such as zircon, baddeleyite, titanite, monazite, apatite, and others; **D)** Magnetic minerals (magnetite, pirrotite, etc.) are removed from the sieved fraction with the use of magnets; **E)** phases with different magnetic susceptibilities are separated with the Frantz magnetic separator; **F)** the fractions with the least susceptibilities are concentrated by immersion into heavy liquids (bromoform, $d = 2.85 \text{ g/cm}^3$; methylene iodate, $d = 3.2 \text{ g/cm}^3$), mainly to separate zircon, baddeleyite and monazite from other phases. Remaining sulfides are washed out by dissolution with HNO₃. A representative sample of zircon (around 100 grains) is then separated manually, using a binocular microscope. The obtained zircon grains are mounted with the aid of an adhesive tape, and fixed onto an epoxy mount, which is then ground and polished to obtain good zircon surfaces for chemical determinations (either with laser ablation, or with electron bombardment in a electron microprobe). Most zircon grains are not homogeneous, so that they have to be submitted to study with a cathodoluminescence technique (CL), to ascertain internal structures (form and extent of a core, if present; types and extent of zonation and its geometry; etc.). In the CPGEOLAB laboratories (IGC-USP), cathodoluminescence studies are performed with a FEI Quanta 250 SEM-XMAX spectrometer (Oxford Instruments), with a magnification interval of 95 to 250 times. More details are discussed in Sato et al. (2014).

Zircon chemistry: determination of major, minor and trace elements by LA-ICPMS. The techniques outlined in Gao et al. (2002) and Yuan et al. (2008) were followed for the determination of the zircon chemistry, using at the same time the expertise gained in our laboratory (Andrade et al., 2010a, 2010b) during determinations of trace elements in several reference minerals and geologic reference rock materials, such as powders BHVO-2G, BCR-2GBIR-1G (cf. USGS 2002), and glasses of komatiites (GOR-128, GOR-132), of basalts (KL-2G, ML-3BG) and of the quartz diorite T-1G (prepared by the Max Planck Institut für Chemie, cf. Jochum et al. 2005).

6. WHOLE-ROCK GEOCHEMISTRY OF SAMPLED GRANITOIDS

The whole-rock geochemical data for the sampled granitoids, as far as available, are listed in Table 1 (Table 1; cf. Electronic Supplementary Tables), together with normative data obtained from the raw chemical determinations, all of them plotted on several widely used chemical diagrams which allow an overview over (normative) petrography and chemical classifications and pinpoint indications of probable environmental features (Figures 17 to 28), always remembering that these samples are representative of the Brasiliano granite genesis and are distributed within a rather tightly limited area (i.e., the basement slices that cover the southeastern portion of the state of São Paulo). The discussion that follows uses obviously a very limited amount of geochemical information about each of the cited granite bodies, a situation that has to be taken into account when reaching conclusions. Nevertheless, the speculation about general geochemical features seems to be valid, and can be used to reach tentative conclusions, which more detailed studies have to validate, or not.

The data set, best observed in the usual Harker diagrams (as a function of silica content; Figure 17), displays variations in a manner that is to be expected in granites worldwide. The values of our granitoids range from 63% SiO₂ to about 75% SiO₂, while contents of total iron oxide (expressed as Fe₂O₃), MgO, and CaO, as well as MnO, show a broadly negative correlation; alkali abundances plot showing an increase with silica content. The other minor elements P₂O₅ and TiO₂ behave in the

same way as MnO, thus indicating, as expected, that most P and Ti are held in accessory and/or mafic mineral phases, also showing a positive correlation between MgO and total iron oxide contents (figure not displayed). The trend in Al_2O_3 variation (Figure 17) is grossly similar in all granitoids, with a slight decrease observed in those rocks with larger silica contents; surprisingly, the Terra Nova sample (TN-1) departs from these projections, presenting a lower than expected alumina content ($<12\%$), in contrast with expectations (more or less constant alumina contents for most true granitoids). The Itaquí enclave (ITQ-E) is an entirely different rock, if interpretations about genesis are correct (namely, it should represent the basic-intermediate counterpart preserved in a “mingling” process with the host granitic liquids).

Figure 17. Harker variation diagrams for major and minor elements, as a function of SiO_2 content. Data belong to the following granite units: ITA-1 and 2: Itaquera; TAP-01 (Taipas, main granite) and TAD-1 (Taipas, dike rock); Pe-04 (Perus tourmaline granite); ITQ-2, 4 (Itaqui main granite); ITQ-E (microgranular mafic enclave in Itaqui); ITQ-D1 (leucocratic dike in Itaqui); MD-24 (satellite stock related to Itaqui); CHA-1 (Ubatuba charnockite); Cant-6 (Cantareira facies); MD-42B (satellite stock of Cantareira); SR-07 (main facies of São Roque granite); ITU-14X (Itu granite); Tico-1, Tico-2 (Tico-Tico rocks), IA-10 (Ilha Anchieta granite).

Thus, major and minor elements, in these plots, show tendencies indicating that similar genetic processes are at work in all these examples, certainly no proof about possible cogenetic origin; minor discrepancies in genesis (e.g., more or less fractionation, or more or less assimilation), are not registered in these Harker diagrams.

More accentuated contrasts, as far as genetic processes is concerned, may be found in Harker plots of trace elements (Figure 18). The elements Zr and Hf show a certain negative correlation with silica increase (mainly indicating, possibly, a decrease in the crystallization of zircons with “differentiation”), while no correlation can be observed in the other plotted elemental diagrams. This can be explained by pointing out that most of the listed elements (with the important exception of Ba, Sr and Eu) are fixed in mafic and/or accessory phases, which do not present a modally simple behavior with evolution in these granitoids.

Figure 18. Harker variations diagrams for some trace elements, as a function of SiO_2 content. For legends, see also Figure 17.

The commonly used TAS diagram (Figure 19, a version taken from Cox et al, 1979) indicates that most of the studied rocks are actually *sensu-latu* granitoids (more accurately, granodiorites to true granites (“monzogranites”), with the exception of the mafic Itaqui enclave (sample ITQ-E), representing the basic extreme in a “mingled” rock system.

Figure 20 shows the classic modal Streckeisen diagram for plutonic rock classification, where the components were here calculated from the normative mineralogy (thus, normative Ab + normative An represent the approximate modal plagioclase). Certainly an approximation, it nevertheless points out the predominance of common “granitoids” among our samples, projected rather closely within a field that represents the position of the supersaturated thermal valley, as determined by experimental work (e.g., Tuttle & Bowen, 1958). Again, the Itaqui enclave stands out, indicating an origin brought about by mingling procedures, far removed from the “normal” evolution of granitoid magmas.

Figure 19. TAS (total alkali-silica) diagram of chemical classification of plutonic rocks (based on Cox et al. 1979; Wilson 1989). The curved heavy line separates the alkaline from the subalkaline rocks. For legends, see also Figure 17.

Figure 20. Normative classification of granitoids in the QAP diagram (after Streckeisen 1974). Plagioclase (P) is the sum of normative Ab and An. For legends, see also Figure 17.

The distribution of alkalis in plutonic rocks is a matter that deserves to be discussed (Figure 21), given the possibility that more extreme compositions are representative rocks of rather special genetic links. Our samples carry proportionally (a little) more K_2O than Na_2O , which suggests that the São Paulo basement was underlain by protoliths which were enriched (in Proterozoic times?) in K_2O , not in Na_2O (for instance, orthogneisses or mafic granulites, instead of gneisses of sedimentary origin?). The diagram also suggests that biotite, not amphibole, should be the predominant mafic phase in the sampled granitoids (as well as in most Brasiliano granitoids, as broadly confirmed by petrographic descriptions).

Figure 22, by its very nature, can indicate those rocks which carry enough alkalis to override the presence of CaO , an oxide instrumental in allowing crystallization of amphiboles and eventually clinopyroxenes, as well as calcic plagioclase. CaO also diminishes with increasing silica content, so that alkali content clearly controls the crystallization of feldspars (enriched in alkalis with increasing silica) and the presence of biotite. It is interesting to note that the two-mica granites (with magmatic muscovite and eventually also garnet, as well as, possibly, tourmaline), such as Itaquerá and Tico-Tico (as well as Perus, Itaqui, and the Taipás dike), plot closely together both in Figures 21 and 22.

Figure 21. The K_2O versus Na_2O contents in the studied granitoids (e.g., LeMaitre 1989). For legends, see also Figure 17.

Figure 22. The MALI (modified alkali –lime index, $\%Na_2O + \%K_2O - \%CaO$) versus silica for the studied granitoids (after Frost et al. 2001). For legends, see also Figure 17.

The rocks indicating, by their mineralogy, an “excess” of alumina are clearly separated in the alumina diagram of Figure 23 (molar A/CNK versus A/NK), such as

the ones carrying tourmaline (Perus), muscovite (Itaquera, Tico-Tico) and garnet (Tico-Tico, eventually Perus). It is interesting to note that many rocks such as Terra Nova, the Taipas main rock and the Cantareira sample (the last ones clearly calc-alkaline granites), as well as sometimes very leucocratic rocks, such as the Taipas dike, plot very close to the alumina saturation (indicated by $A/CNK=1.0$), thus indicating that alumina, potash and soda are present in this rock in almost stoichiometric proportions to form feldspars; biotites in the cited rocks should be practically devoid of excess alumina. As a contrast, biotites in most granitic rocks, worldwide, are probably of a “peraluminous” type, in the sense that they are relatively enriched in Al (cf. White 1992).

Figure 23. The alumina indices A/CNK versus A/NK (molar proportions) for the studied granitoids (Maniar & Piccoli 1989). For legends, see also Figure 17.

Enrichment of FeO relative to MgO has been recognized to cause differences between rock suites. The ones enriched in Fe are referred to as representing the “Skaergaard” trend, those enriched in Mg as the “Cascade” trend, or, more usually, respectively referred to as the “tholeiitic” and “calc-alkalic” suites. Miyashiro (1970) showed that rocks following these distinct trends could be distinguished on a plot of $[FeO/(FeO + MgO)]$ against SiO_2 , where FeO values correspond to measured $Fe^{2+}O$ in the respective rocks. Later on, it was established that Miyashiro’s iron number could be replaced by FeO_{total} (i.e., total iron calculated as FeO , the Fe-number cited

in Frost et al, 2001, when separate data for FeO and Fe₂O₃ are not available). Figure 24 shows a plot of silica content against Fe*, a modified $[\text{FeO}_{\text{tot}}/(\text{FeO}_{\text{tot}} + \text{MgO})]$ index). The enrichment of FeO relative to MgO has also been used to distinguish between granitoids from different tectonic environments. In particular, suites with A-type characteristics are distinctly more enriched in Fe than the Cordilleran-type granitoids (Maniar and Piccoli, 1989; Frost and Frost, 1997). The Ferroan granitoids or tholeiitic suites are here represented by the charnockite CHA-1, the peraluminous two-mica Tico-Tico (01 and 02), and Itaquera samples (ITA-02, 04), together with the Perus tourmaline granite (Pe-04), and also the Terra Nova (TN-1) sample, the leucocratic dike in Taipas (TAD-01), and the Itu granitoid (ITU-14X), while the others are classified as belonging to a magnesian or calc-alkaline suite .

Figure 24. Ferroan features of the studied granitoids (Fe* versus SiO₂, after Frost et al, 2001). For legends, see also Figure 17.

One of the most used diagrams for the definition of tectonic environments is the one proposed by Pearce et al., 1984, based on the contents of Rb versus (Y + Nb) (Figure 25). Our granites are mostly represented at the confluence of the three most extended fields, represented by volcanic arc, within-plate and syn-collision granites (with the exception of the Taipas dike rock, representing possibly accumulated liquid by local inflow into a dilatational fracture).

The discriminating diagram presented in Figure 25 shows that the majority of the granites here analyzed plot in the post-collision field (Pearce, 1996). These granites are the most difficult to classify because they were derived from a large range of protoliths. In general, it is supposed that they originate, ultimately, from enriched mantle sources (through complex subduction and/or intraplate processes), and therefore associated to widespread crustal interactions.

Figure 25. Tectonic environmental diagram Rb versus (Y + Nb), for the studied granitoids (after Pearce et al. 1984), including field for post-collision granitoids (Pearce 1996). For legends, see also Figure 17.

According to Whalen et al (1987) and Eby (1990), the type-A granites define a distinct group within the granite family, supposed to have crystallized from high temperature melts, parameters which are not normally achieved in the crust. Hence, the involvement of mafic magmas, or high mantle heat flow, seems to be a necessary condition for their formation. Generally, they are characterized by higher Fe/Mg and Ga/Al ratios, the result of extensive feldspar fractionation, and abundance in incompatible trace elements, stabilized in magmas by Cl and F. Diagrams which can classify the granites into several of the currently accepted genetic types, such as “S”, “I”, or “A”, are constructed using several trace elements indicators (Whalen et al. 1987; Eby, 1990), some of which are used here to separate fractionated from unfractionated I and S-type granites and these from the A-type. These diagrams use

the following data: FeO/MgO versus 10000Ga/Al (Figure 26a), FeO/MgO versus Zr+Nb+Ce+Y (Figure 26b), (K₂O+Na₂O)/CaO versus Zr+Nb+Ce+Y (Figure 26c) and 10000Ga/Al versus Zr+Nb+Ce+Y (Figure 26d). Our samples plot in different fields, such that samples from Tico-Tico, Perus and Ilha Anchieta can be classified as type A, while the others correspond mostly to the I or S lineages, or more fractionated I-S types. Indices in Figure 26c and Figure 26d show, on the other hand, that the samples from Ilha Anchieta, Ubatuba charnockites, Itu, Itaqui (principal granite; enclave), Itaqui satellite, and São Roque plot within the A-type field. Tico-Tico and Perus would be considered I-S “felsic fractionated” types. A cursory observation of these results indicates that geochemical indices would classify these granites as very different genetic types. Obviously, these chemical indices, although widely cited in the literature, may not capture entirely the complexities inherent in granite petrogenesis.

Figure 26a-d. Genetic classification diagrams for the studied granitoids, based on the indices $\text{FeO}_{\text{total}}/\text{MgO}$ vs. $(10000\text{Ga}/\text{Al})$ and vs. $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$, $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{CaO}$ vs. $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$, and $(10000\text{Ga}/\text{Al})$ vs. $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$, after Whalen et al. (1987) and Eby (1990). UG: unfractionated M-, S-, I-type granites; FFG: Fractionated Felsic granites. For legends, see also Figure 17.

Figure 27 presents a REE diagram (normalized against C1-chondrite) of all analyzed granites, immediately presenting two types of rocks, those that present Eu anomalies (therefore, fractionation controlled at least in part by feldspars) against

other types with no Eu anomaly (“non-fractionated” types). The following granites belong to the first fractionated group: Itaquera, Perus, Itu, Terra Nova and Tico-Tico (mostly, “S-type” granitoids according to mineralogy), while the rocks from Itaqui, Cantareira and Taipas (main porphyritic facies) are “unfractionated” (i.e., no Eu anomaly). A special rock is the TAD-01 sample (represented by the Taipas dike rock, filling in a supposedly dilatational fracture), which shows a positive Eu anomaly (hence, enrichment in Eu), different from the smooth tendency expressed by the main TAP-01, with no Eu anomaly. Diagrams shown by other authors dealing with some of the same rock types here presented are somewhat different from our figures (e.g., lesser amounts of REE, no Eu anomaly; e.g. Wernick et al., 1996) while diagrams in Morteani et al. (2008) are very similar to the ones shown here. The overall tendency is that of a moderate enrichment in LREE (usually, up to about 100 times; Figure 27), with a normalized Ce/Yb ratio of about 20 to 40, a quotient that probably indicates that garnet-holding residues of melting are present at depth.

Figure 27. Normalized REE patterns for the studied granitoids (normalized against C1 chondrite; values from Sun & McDonough, 1989). For legends, see also Figure 17.

processes would be to compare some trace element ratios such as the ones using Eu and Sr, both attracted by plagioclase but showing different behaviour in igneous and sedimentary environments. During fractional crystallization, or partial melting, both Eu and Sr are fractionated into plagioclases, presenting decreasing ratios in the liquids that eventually coexist with feldspar-holding rocks. Europium contents also decrease in comparison with other trivalent REE, since the reduced Eu^{2+} ion will enter preferentially the plagioclase structure, therefore explaining the origin of the progressively enhanced negative Eu anomaly in REE normalized diagrams of many igneous rocks, a situation that can be equally revealed by the diminishing Eu/Sm ratio (Kemp & Hawkesworth, 2003).

In sedimentary processes, Sr set free from the plagioclase structure is carried away by water (e.g., in diagenetic interstitial solutions and during lithification), while bivalent Eu, in these environments, oxidizes into insoluble Eu^{3+} and will therefore be retained in sediments. Weathering will thus not diminish the amounts of Eu in comparison with Sm, so that the ratio Eu/Sm will show a divergent behavior depending on the controlling processes (igneous or sedimentary).

On the other hand, Rb is generally retained in clay minerals during weathering. While it behaves as an incompatible element in igneous processes, concentrating in the liquid, strontium is captured within the feldspar structure (a compatible behaviour), so that the Rb/Sr ratio can become a valuable indicator about the controlling process. Kemp & Hawkesworth (2003) proposed to use the ratios Rb/Sr, Eu/Sm and Eu/Sr as a means to depict the importance of igneous or sedimentary processes in the generation of protoliths (whether purely of igneous or of sedimentary origin, or a mixture of both) from which the granitoids magmas were derived.

The ratios Rb/Sr versus Eu/Sr, and Eu/Sm versus Eu/Sr of whole-rock analysis for our studied granitoids are depicted in Figure 29 (a and b), suggesting that samples Cant-6 (Cantareira) and MD-42B (Cantareira “satellite”), as well as ITQ-2, ITQ-4, MD-24 and ITQ-E (Itaqui main granite, “satellite” and enclave), and SR-07 (São Roque) represent non-fractionated granitoids, in comparison with the Bulk Crust (BC) composition. On the contrary, samples Tico-2 (Tico-Tico), ITA-2 (Itaquera), ITU-14X (Itu), TN-1 (Terra Nova) and ITQ-D1 (Itaqui dike) are more differentiated than the BC ratios, showing decrease in the Eu abundances relative to the Sm contents, as

Eu^{2+} content is reduced by uptake within the plagioclase structure. The marked increase in the Eu/Sr ratio suggests that Eu^{2+} capture is more effective than the partitioning of Sr into plagioclases.

Sample ITQ-D1 (Itaqui dike) is the most fractionated within the plotted samples, but under more reduced conditions than the main Itaqui granite (samples ITQ-2 and -4), given that oxidation increases the abundance of Eu^{3+} . The Perus sample (Pe-04) was possibly generated by fractionation from magmas similar to the ones that crystallized to form the Itaqui, Taipas and Cantareira occurrences; it was however more oxidized than the Itaqui dike magma (sample ITQ-D1). This very fractionated magma may have been subjected to additional processes such as mixing with other fluids thus generating a chemical fingerprint pointing to interference with sedimentary processes in the respective protoliths and/or late control of additional fluids, thus explaining the drift of the plots of the cited samples (including the most extreme case, Perus) to fields with lower Eu/Sm and higher Eu/Sr; the explanation being that Eu was retained in clays and ultimately in feldspars (during the passage of sedimentary rocks into recrystallized ones), while Sr was drained away during the early history of the corresponding protoliths by sedimentary processes. Sample TAD-1 (Taipas dike) plots in a different area, with lower Eu/Sr and higher Eu/Sm and Rb/Sr ratios, presenting a positive Eu anomaly, suggesting an evolution by previous extraction (crystallization) of at least some plagioclase and the possibility of forming very fractionated liquids.

The samples ITQ-E, ITQ-2 e 4, MD-24 (Itaqui main rock and enclave, Itaqui “satellite”), TAP-1 (Taipas main rock), SR-06 (São Roque), Cant-6 and MD-42B (Cantareira, “satellite”) plot in the Rb/Sr area with ratios (0.1 to 0.3) comparable with BC, while samples ITA-1 and 2 (Itaquera), Itu-14X, Tico-1 and 2 (Tico-Tico) and TN-1 (Terra Nova) present much higher Rb/Sr ratios and a more evolved chemical profile. This behavior, as indicated before, may be related to control by weathering processes for the corresponding protoliths, maintaining Rb abundances in the original clay minerals while extracting the more soluble Sr from the weathering residue. An extreme case is that of TN-1 (Terra Nova), similar in some indices with the mean A-type LFB granite, showing the lowest Sr and Rb values (2.7 and 82 ppm, respectively), and very low values of MgO , $\text{Fe}_2\text{O}_{3(\text{total})}$, CaO , as well as Al_2O_3 and TiO_2 (Figure 17).

The sample ITQ-D1 (Itaqui dike) presents a Rb content (251 ppm) twice as large as that of the main Itaqui granite (ITQ-2 and 4; around 104 ppm); Sr abundances are, respectively, 58 and 763 ppm; Table 1). This behavior may suggest that this dike is somewhat different, genetically, than the sample representing the main granite ITQ -2 and -4 (as also the Itaqui enclave ITQ-E; normative proportions of K-feldspar and plagioclase in these rocks are very similar). Sr decrease in these crystallizing magmas is controlled by uptake in plagioclase, that of Rb by fractionation within K-feldspar; probably, Rb/Sr ratios should not change drastically during crystallization of both feldspars in the residual magmas. It is to be observed that Rb in the Itaqui dike is as high as in Perus (Pe-04), Itaquera (ITA-1 e 2) and Tico-Tico (Tico-1 and 2); Sr contents are also similar (Table 1). The charnockite sample CHA-1 is very different from the other granitoids samples, similar in composition to the BC analysis (Figure 29), with an almost identical Eu/Sm ratio, but higher Eu/Sr, possibly on account of a relative decrease in Sr, showing a behavior that would suggest a contribution by meta-sedimentary protoliths.

Figura 29. Plots of Rb/Sr versus Eu/Sr (part **a**) and Eu/Sm versus Eu/Sr (part **b**) for the studied granitoids. For comparative purposes, the corresponding ratios of the Bulk Crust, the mean for A type granites from the Lachlan Folded Belt (LFB) and the values proposed for the A-type granitic Padthaway occurrence, SE Australia (Rudnick & Gao. 2003).

7. ANALYTICAL RESULTS FOR ZIRCONS

About 100 to 150 zircon grains were separated from each of the ground samples, with a final separation controlled by density methods (cf. section 5.3). The mounted and polished zircon grains were then subjected to cathode-luminescence with a SEM (scanning electron microscope), as well as simple optical observations under transmitted light (TL), to detect possible zoning patterns, which could lead to interpretations about growth history of the selected grains (e.g., core with a different texture than the outer zone, or zones, possibly indicating an inherited character, a residue of a relictic grain already present in the melting protolith; outer zone, or zones, as possible additions during magmatic growth; etc.). The determination of zircon chemistry was performed later on, using the laser-ablation methodology already cited in section 5.3. Results are presented below.

7.1. Cathodo-luminescence and transmitted-light observations on grains in mounted samples

Figure 30 (Figure 30; cf. Electronic Supplementary Figures) presents photographs of mounted zircons as observed mostly under cathodoluminescence for the studied zircons, in the following order : samples from Cantareira (Cant-6), Itaquí (ITQ-2, “satellite” intrusion of Cantareira (MD-42B), “satellite” Itaquí intrusion (MD24), Taipas (TAP-1), Tico-Tico (Tico-2), São Roque (SR 07), Itu (Itu-14X), Terra Nova (TN-1), Ubatuba charnockite (CHA-1), Ilha Anchieta (IA-10), Perus tourmaline sample (Pe-04), Itaquí enclave (ITQ-E), Itaquera (ITA-2), Taipas dike (TAD-1).

Some samples present predominantly elongated prismatic grains, with little color or with a faint yellowish-brownish tone (Cantareira Cant-6 and MD-42B; Itaquí (ITQ-2; and MD-24); Taipas (TAP-1 and TAD-1); Tico-Tico (Tico-2); São Roque (SR-07); Ilha Anchieta and Ubatuba charnockite (IA-10, CHA-1). In other samples, less elongated and more equant zircons may appear in considerable amounts, together with more elongated forms (e.g., Itu-14X; Terra Nova TN-1; Perus Pe-04; Itaquera ITA-2; Itaquí enclave ITQ-E; Taipas dike TAD-1). Very white cores of zircons are observed in samples Pe-04 (Perus) and Terra Nova (TN-1), thus indicating possibly higher contents of U, Y, and HREE (Figure 30).

Sizes usually vary between 50 and 400 μm , frequently very similar in most samples (see Figure 30).

Many grains present complex oscillatory zoning, possibly characteristic of magmatic crystallization, also showing in some cases somewhat darker cores (e.g., ITU-14X, SR-07 e ITQ-E) or, more commonly, darker intermediate or outer zones (e.g., Cant-6; ITQ-2, TAP-1, TAD-1, Tico-2; Per-04, TN-1).

7.2. Trace element chemistry in zircons: results

Table 2 (Table 2; cf. Electronic Supplementary Tables) presents the results obtained from zircons separated from the studied samples. The complete array of REE were determined, as well as Ba, Sr, Rb, Th, U, Nb, Ta, P, Ti, Zr, Hf, and Y. Data are presented in several ways, as usually depicted in the literature. A first array shows variograms (Figure 31), indicating the variations (and similarities, in most

cases) present in the trace-element geochemistry of zircons in our granites: in these diagrams, the following elements are presented, in the cited order: Ba, Rb, Th, Nb, Ta, La, Ce, Sr, Nd, P, Sm, Zr, Hf, Ti, Tb, Y, Tm, Yb, normalized against C1-chondrite (McDonough & Sun 1995).

Cant-6

MD-42B

ITQ-2

ITQ-E

TAP-1

TAD-1

ITU-14X

Figure 31. Variograms (spidergrams) obtained for the studied zircons, with values normalized against C1-chondrite. Represented samples are Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Zircon is, of course, the primary host mineral containing Zr and Hf, two elements which are always correlated in the presented diagrams, as expected. The highest amounts of Hf are found in ITA-2 (11000-14000 ppm), Tico-2 (10000-20000 ppm), TN-1 (8500-21000 ppm) and Pe-04 (20000-38500 ppm), while most samples show contents varying from 8000 to 13000 ppm. These higher ratios suggest that the host granites are relatively evolved rocks, derived from differentiated magmas, given that in most cases granite evolution follows a path of Hf enrichment with differentiation (Hoskin & Schaltegger 2003).

Crustal materials, in general, maintain a Zr/Hf ratio close to 35-40, the ratio found in the chondrite (Weyer et al. 2002). Most of the studied samples, however, present ratios somewhat above the chondritic value (cf. Table 2, Electronic supplementary tables). Granites Cant-6 and MD-42B (Cantareira), CHA-1 (charnockite), IA-10 (Ilha Anchieta), ITQ-2, ITQ-E, ITQ-D, MD-24 (Itaqui), TAP-1 (Taipas), SR-07 (São Roque), and ITU-14X (Itu), show ratios between 42 and 50, while samples Tico-2 (Tico-Tico) and ITA-2 (Itaquera) present Zr/Hf ratios around 40 (with high dispersion, values from 23 to 55, and 34 to 46, respectively); samples TN-1 (Terra Nova) and Pe-04 (Perus) yield values of 33 and 19, below the chondrite average.

Figure 32 presents the REE diagrams, normalized to C1-chondrite (Sun & McDonough 1995). Individual results for several grains are plotted, as well as the corresponding mean and median values.

Cant-6

MD-42B

ITQ-2

ITQ-E

TAP-1

TAD-1

MD-24

Pe-04

SR-07

ITA-2

TN-1

Tico-2

CHA-1

IA-10D

ITU-14X

Figure 32. REE diagrams obtained from various zircon grains for the cited samples, as well as the corresponding mean values. C1-chondrite normalized according to Sun & McDonough (1995)

Table 3 presents ratios often used to define REE and trace elements trends in magmatic rocks, which will be used to separate these granite samples into possible different geochemical groups.

It is interesting to note that the main features in Figure 31 repeat themselves in the diagrams, all of them presenting systematic peaks for (from left to right) Th, Ce, Nd, Zr and Hf (the last two elements being geochemically correlated) and, similarly, depletions for La, Rb, Sr, P and Ti, thus presenting (Figure 31) more similarities than differences. It is difficult to explain the Ce and Nd peaks, except perhaps on account of the relative easiness which allows these elements to enter the zircon structure, dominated by HFSE such as Zr and Hf. The same reasons probably apply for Th, a natural partner for elements in structures holding Zr (e.g., zircon, baddeleyite).

This behavior is certainly dictated, in the first place, by crystallochemical reasons, controlled by the structure of the host mineral. All granitic magmas show certain geochemical similarities, as far as enrichment and depletion of elements is concerned. Hence, an increase in the abundances of some HFSE in the granitic magmas should induce an uptake of these elements by phases such as zircon (e.g., Th and U).

More than indicating the general similarities, it should be useful to observe the differences, which will probably reflect the relative *enrichment* (or *depletion*) of some elements such as the REE and, to a certain extent, the *crystallization conditions of the magmas*, assuming that the final zircon trace-element chemistry is entirely governed by magmatic crystallization (as suggested, for instance, by textural means, e.g., zoning behavior). Samples such as Terra Nova (TN-1), Itaquí “satellite” (MD-24), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), charnockite (CHA-1) and Perus (Pe-04) show a remarkable lack of dispersion (as compared to behavior in Itaquera, Tico-Tico, Cantareira “satellite”, Itaquí enclave and Itu, with wider variations; cf. Figure 31). The uniform chemistry in these variograms is to a certain extent repeated in the REE diagrams (for instance, relative REE constancy in samples from Taipas main rock TAP-1, Ilha Anchieta IA-10 and Perus Pe-04, but showing wider variations in others; cf. Figure 32).

During magmatic crystallization, probably the zircon grains showing larger chemical variations crystallized, from beginning to end, under somewhat different conditions (e.g., variations in fluid fugacities, or heterogeneous diffusion of elements

in the magmas, or greater mobility of zircon crystals in the melt, traversing probably different magma batches in a somewhat heterogeneous magma chamber; etc.). On the other hand, the remarkable uniformity shown by the zircon grains with rather constant trace-element chemistry should indicate surprisingly uniform crystallization conditions.

Table 3: Summary of intervals and median values for REE contents and ratios: $(Yb/La)_N$, $(Yb/La)_N$, $(Yb/Gd)_N$, $(Sm/La)_N$, Ce/Ce^* , Eu/Eu^* , LREE and total sum of REE (in ppm), abundances of Th, U, Y, Hf (in ppm) and ratio Th/U for the samples listed in Table 2 (Electronic Supplementary Tables).

	$(Yb/La)_N$		$(Yb/Gd)_N$		$(Sm/La)_N$		$(Ce/Ce^*)_N$		$(Eu/Eu^*)_N$		LREE _N		REE(tot) ppm	
	range	median	range	median	range	median	range	median	range	median	range	median	range	median
CHA-1	1327-54134	10531	6.9-29.4	15.5	52-848	194	6.0-124	37.0	0.04-0.26	0.15	7.6-29.35	20.5	451-1460	757
TAP-1	907-5534	1966	7.9-28.5	14.5	11.6-122	38.5	17.5-68.7	34.0	0.65-1.2	0.78	18-70	30	153-613	368
MD-24	23-8537	1357	3.9-43	21.9	4.9-117	17.1	3.0-184	32.5	0.6-1.2	0.87	30-337	50	274-777	421
IA-10D	182-2086	920	6.6-23.8	11.3	2.0-246	26.5	7.7-22.0	12.8	0.11-0.43	0.27	30.0-68.5	44.2	349-1032	718
ITQ-E	52.2-2706	498	5.7-48.4	28.9	1.0-112	4.8	2.6-138	12.3	0.27-1.03	0.72	34.7-3844	74.9	330-7236	584
TAD-1	25-3160	472	2.8-31.9	9.9	2.1-27.8	17.5	2.3-60.9	11.7	0.42-1.47	0.65	10.3-220	43.7	74-684	465
Tico-2	0.73-12154	427	0.18-308	10.7	2.98-31.8	13.9	2.2-16.8	4.8	0.09-0.31	0.16	14-12056	37	358-19675	737
MD-42B	4.1-1978	286	2.2-43.7	13.5	3.8-38.1	9.25	1.98-25.8	9.1	0.6-1.11	0.85	22-1441	45.4	177-1653	275
SR-07	1-922	138	1.2-52.7	15.7	2.3-13.0	6.4	1.9-24.2	5.9	0.50-1.85	0.65	59-3721	91	338-3821	488
ITA-2	4.3-773	89.8	1.8-35.8	11.7	1.2-11.0	3.22	1.05-6.52	1.8	0.06-0.42	0.21	86-2637	234	1033-4665	2033
Cant-6	4.9-2310	59.8	0.9-23	4.73	5.4-70.3	10.3	1.9-63.0	4.3	0.64-1.10	0.97	23-1158	187	89-1480	578
ITQ-2	1.0-2200	48.2	6.9-44.0	21.6	1.8-15.6	2.51	1.6-34.7	3.0	0.5-1.1	0.67	55-4793	274	517-1430	779
TN-1	9.7-3164	47.9	0.63-63.9	2.79	4.5-32.6	12.8	3.1-18.6	3.2	0.11-0.27	0.23	277-11576	3134	3218-27770	11127
Pe-04	33-556	58.2	2.2-41.7	3.73	6.0-10.0	9.1	4.0-7.4	4.9	0.19-0.25	0.19	3545-10394	6858	18555-31565	22673
ITU-14X	9.2-6009	35.2	1.4-57.4	9.67	1.89-213	6.79	1.6-66.5	2.6	0.23-0.59	0.4	44-2981	734	620-4197	1536
	U (ppm)		Th (ppm)		Y (ppm)		Hf (ppm)		Th/U	observed accessory minerals				
	range	median	range	median	range	median	range	median						
CHA-1	60-300	237	35-202	130	652-2145	1093	9551-11568	10566	0.549	zircon(zr), monazite (mnz), apatite(apt)				
TAP-1	110-310	145	48.7-206	85	219-929	532	10948-13468	11719	0.586	zr, apt, titanite(tit)				
MD-24	159-434	224	92-404	164	316-931	528	9887-12903	10954	0.732	zr, tit, apt				
IA-10D	66-558	228	78-232	185	412-1489	1007	8674-12927	9507	0.811	zr, tit, apt				
ITQ-E	370-8426	645	116-48705	228	378-7383	702	8095-12737	11271	0.353	zr, tit, apt				
TAD-1	82-260	147	52-171	120	381-978	627	8910-12035	10813	0.816	zr, tit, apt				
Tico-2	70-5131	302	28-684	134	578-21352	1210	8994-21295	11002	0.444	zr, apt, granada(??)				
MD-42B	164-423	306	81-219	118	297-843	384	10714-13308	11779	0.386	zr, tit, apt				
SR-07	357-1968	413	232-1478	293	399-1831	569	9771-12748	10949	0.709	zr, tit, apt				
ITA-2	656-3166	1556	198-2093	1106	1479-4614	3125	10704-14474	12787	0.711	zr, mnz, apt				
Cant-6	109-903	415	56-398	196	106-1794	716	9870-13358	11833	0.472	zr, apt, tit, allanite (aln) or epidote (ept??)				
ITQ-2	236-1425	676	205-1906	361	414-1791	799	9110-12651	11400	0.534	zr, tit, apt				
TN-1	677-4213	2175	534-7094	3111	4826-32386	13729	8477-21005	11084	1.430	apt, tit, zr (white and yellowish)				
Pe-04	6785-16284	9160	428-2685	1089	30856-54202	37806	20015-27085	23628	0.119	zr, apt, tit, turmaline (tur)				
ITU-14X	70-1043	513	91-1672	666	800-3834	1364	8479-14392	10473	1.461	zr, apt, tit				

The *total abundance of REE* varies broadly in these zircons, but the most remarkable values are found in Pe-04 (Perus, 18555 to 31565, median 22673), TN-1 (Terra Nova, 3218 to 27770 ppm, median 11127 ppm), ITA-2 (Itaquera, 1033 to 4665 ppm, median 2033 ppm), and ITU-14X (Itu batholith, 620 to 4197 ppm, median 1536 ppm)

Most of the studied grains in the various granitic samples show a *marked predominance of LREE* (normalized figures), always above 10 times chondrite, a limiting value expected to be present in igneous zircons (Hoskin & Schaltegger 2003). *MREE abundances*, such as Gd_N , are remarkably enriched above chondrite values in samples IA-10D (Ilha Anchieta) and CHA-1 (charnockite, the last two samples with enrichment factors between 50 to 500), SR-07 and ITQ-E (São Roque and Itaquí enclave; 50-1000), ITU-14X (Itu batholith), and ITA-2 (Itaquera), the last two with enrichment factors for Gd_N between 100 to 1000. Even larger enrichment is observed in samples TN-1 (Terra Nova; enrichment between 1000 to 10000), and Tico-2 (Tico-Tico) and Pe-04 (Perus tourmaline sample: enrichment for both by a factor of 10000 to 100000). Enrichment by a factor of 10^3 to 10^4 (times chondrite) in the HREE, especially when Yb_N is considered, is also remarkable, an expected behavior for many zircons crystallized in granites (Hoskin & Ireland 2000; Hoskin & Schaltegger 2003; Wang et al. 2012).

The REE diagrams (Figure 32) show large variations in the $(Yb/La)_N$ ratios, depicting somewhat different inclinations from LREE to HREE; e.g., with a median value of 10531 (from 1321 to 54134; sample charnockite CHA-1), 1966 (from 907 to 5534; Taipas TAP-1), 1357 (from 23 to 8537; MD-24), 920 (from 182 to 2086; Ilha Anchieta IA-10D). A less pronounced drop in values for the $(Yb/La)_N$ ratios can be observed in samples ITQ-E (Itaquí enclave), TAD-1 (Taipas dike), MD-42B (Cantareira “satellite”), Tico-2 (Tico-Tico), and SR-07 (São Roque). Decline in values from LREE to HREE is more pronounced in the charnockite CHA-1 than in the IA-10D sample (Ilha Anchieta), although the total abundance of REE in both samples are practically identical (median value of 775 ppm, from 451 to 1460 ppm for the charnockite, to a median of 718 ppm, from 349 to 1032 ppm for Ilha Anchieta).

In these variation diagrams (Figure 32), remarkable *positive Ce peaks* are observed in samples from Cantareira (Cant-6, MD-42B), Itaquí “satellite” (MD-24), Taipas main rock (TAP-1), Itaquí enclave (ITQ-E), charnockite (CHA-1), and others.

The largest Ce/Ce* [Ce* = (La_NxNd_N)^{1/2}] anomaly values are registered for samples CHA-1 (charnockite), TAP-1 (Taipas main rock), MD-24 (Cantareira “satellite”) and IA-10D (Ilha Anchieta) (respectively 37, 34, 32, 13). The positive anomaly for this element represents crystallization under oxidized conditions (high oxygen fugacity), most notably observed in the cited samples, favoring the change from Ce³⁺ to Ce⁴⁺, the last ion substituting for Zr in the zircon structure. Typical values of the Ce/Ce* ratios in these anomalies should vary between 1 and 10 for granitic rocks, but may reach higher values in zircons from pegmatites and syenites (2 to 300; Belousova et al. 2002; Clairbone et al. 2010; Trail et al. 2012).

The *positive Ce peaks*, indicating oxidizing crystallization, are clearly present as a *single anomaly* in various samples from Cantareira main rock and “satellite” (Cant-6, MD-42B), Itaqui main rock, “satellite”, enclave (ITQ-2, MD-24, ITQ-E), and Taipas main rock (TAP-1), thus indicating for most of the zircon grains a crystallization under higher oxygen fugacity. These rocks should be separated from those crystallizing *entirely* under more reduced conditions, especially when marked by a negative Eu anomaly (hence, formation and withdrawal of Eu²⁺). This situation has not been observed in any of the analyzed samples. In this context, it is interesting to observe those samples presenting both the positive Ce anomaly as well as the negative one depicted by Eu behavior (samples Itu, ITU-14X; Terra Nova, TN-1; Itaquera, ITA-2; Ilha Anchieta, IA-10D; charnockite, CHA-1; Perus, Pe-04; Figure 32). An explanation for this could be as following: crystallization may have occurred under oxidizing conditions, then changed to one where reduced conditions were dominant (or vice-versa). A textural control of the analyzed spots within the crystal morphology could tell which condition prevailed in the first place, to be replaced later on by the opposite condition. In some samples, the REE diagrams show that the oxidized behavior (high oxygen fugacity) controlled part of the zircon grain formation showing a positive Ce spike (restricted to some grains), passing to a behavior with an entirely or at least partly smooth variation in normalized REE abundances (as shown by other grains in the same sample; e.g., samples Cant-6 from Cantareira, ITA-2 from Itaqui, SR-07 from São Roque, ITU-14X, from the Itu batholith; Figure 32).

Clear *negative Eu anomalies* are present in most analyzed grains in samples from Tico-Tico (Tico-2), Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha

Anchieta (IA-10D), charnockite (CHA-1), and Perus (Pe-04), but are almost entirely absent in Cantareira (Cant-6, MD-42B), Itaquí (ITQ-2, MD-24), São Roque (SR-07), Taipas (TAP-2, TAD-1) and the Itaquí enclave (ITQ-E). Samples CHA-1 and IA-10D register the largest negative Eu/Eu* ratio (respectively 0.15 and 0.27), which are considered typical values for fresh magmatic zircons (Hoskin & Schaltegger 2003). This similar behaviour is also observed in samples ITA-2, TN-1, Tico-2, Pe-04 and ITU-14X. This marked negative anomaly for the element may be explained by another parameter, reflecting the important control over element distribution created by feldspar crystallization (previous to zircon appearance, or during its crystallization), since Eu^{2+} enters the feldspar structure as a substitution for Ca^{2+} .

Figure 33. Variation diagrams of total REE, Y, U and Th versus Hf for the analyzed samples. Hf is taken as a differentiation index (Hoskin & Schaltegger 2003).

Figure 33 shows how most of the determinations of total REE, Y, U and Th on zircon grains (plotted against Hf) cluster around 500 to 10000 ppm (for total REE and

Y), and around 100 to almost 10000 for both Th and U, therefore with no indication of correlation for the respective sample population; Hf median values in all cases are around 12000 for these clusters. Overall median U and Th abundances are around 150 to 300 ppm and 100 to 200 ppm, respectively, but presenting varying proportions, sometimes showing strongly enriched zircons in U and Th (e.g., medians of Pe-04 from Perus record Th= 1089 ppm, U=9160 ppm; ITA-2 from Itaquera, Th= 1106, U=1556 ppm; TN-1 from Terra Nova, U=2175 ppm, Th= 3111 ppm; these granitoids, as well as sample from the Itaqui enclave ITQ-E are the ones presenting the highest U and Th contents in zircons; cf. Table 3).

On the whole, the variations observed in element abundances in zircons from the same granite are very variable, frequently providing difference in abundances over an order of magnitude (cf. also discussion in Pettke et al. 2005; Li et al. 2012). However, some outliers are present (Figure 33), spreading out in a linear fashion, as visible especially for zircons from the Perus tourmaline granite (Pe-04), Tico-Tico (Tico-02) and Terra Nova (TN-2), indicating that high Hf abundances (>14000-15000 ppm) favour (even if slightly) the uptake of the cited elements (U, Th).

The uptake of Hf in the zircon structure seems to be dependent on temperature of the magmas, more than its composition (Clairborne et al. 2006; Watson et al. 2006; Bolhar et al. 2008). In this sense, it is interesting to compare the presence of Hf with the Th/U ratio for zircons from several samples (Figure 34). Although most of the diagrams present the data distributed as clusters, with little or no visible correlation, some slightly (negative) correlation can be observed between these two indices (Figure 34), especially in Cant-6 (Cantareira), IA-10D (Ilha Anchieta), ITQ-2 (Itaqui), TAP-1 and TAD-1 (Taipas main granite and dike), and SR-07 (São Roque).

HFS elements Nb, Ta, and Ti can substitute Zr in the zircon structure, presenting typical values which, according to the literature, should be as indicated: $Nb \leq 62$ ppm, $Ta \leq 3$ ppm and $Ti \leq 75$ ppm (Hoskin & Schaltegger 2003). Our data show a wider variation, such as listed in Table 4, than the range cited in the literature, as especially visible by the behavior of the Perus tourmaline granite, Pe-04, admittedly a much differentiated granite; our intervals are also remarkably higher than the figures cited in the literature.

Cant-6

MD-42B

TAP-1

TAD-1

MD-24

ITQ-2

ITQ-E

Pe-04

SR-07

ITA-2

ITU-14X

Tico-2

CHA-1

IA-10D

TN-1

Figure 34. The ratio Th/U versus Hf, the last element taken as a differentiation index, for zircons from most of the studied granitoids.

For instance, the determined range of values in Pe-04 for Ta is 142 to 583 ppm, Nb from 2024 to 6890 ppm, and Ti between 13 and 485 ppm. Values for Nb and Ta are also somewhat higher as the literature values in sample TN-1 (Terra Nova), ITU-14X (Itu batholiths) and ITA-2 (Itaquera). Van Lichtenvelde et al. (2007, 2009, 2011) attribute these higher values in Ta to the presence of magmas enriched in the element, which can enter the zircon structure before the possible crystallization of phases holding Ta as a constituent element (e.g., tantalite, etc.), an exchange probably also driven by coupled reactions, such as $Al^{3+} + Ta^{5+} = 2 Zr^{4+}$. On the other hand, Belousova et al. (2002) favor a hypothesis whereby La (and other similar elements) are introduced into zircon by means of coupled reactions such as $(REE,Y)^{3+} + (Nb,Ta)^{5+} = 2 Zr^{4+}$, or $(REE,Fe)^{3+} + (Nb,Ta)^{5+} = 2 Zr^{4+}$.

Table 4. Contents of elements Nb, Ta and Ti determined in zircons from samples Cant 6, MD-42B, ITQ-2, ITQ-E, ITQ-D1, IA-10D, CHA-1, MD-24, TAP-1, SR-07, ITU-14X, Tico-2, ITA-2, TN-1 and Pe-04.

Sample	Nb (ppm)		Ta (ppm)		Ti (ppm)		Nb/Ta
	range	median	range	median	range	median	
Pe-04	2024-6890	3517	142-583	254	13-485	75	13
TN-1	59.9-1229	415	4.0-69.1	10	7.4-1075	297	41
ITU-14X	3.0-109	38	0.5-14.5	4.4	4-485	79	7
ITA-2	19.0-314	32	2.7-14.5	5.5	3.2-155	13	6
CHA-1	9.9-13.1	12	0.3-1.9	1.0	3.3-11.9	6.3	12
ITQ-2	10.1-17.9	12	0.17-1.1	0.37	2.2-129	8.0	31
SR-07	10.1-34.0	11	0.15-10.7	0.34	3.1-134	12	33
TAP-1	10.0-12.7	11	0.13-0.46	0.32	2.0-11.3	3.6	35
IA-10D	10.3-12.5	11	0.65-1.5	0.95	7.2-25.3	16	11
MD-24	9.1-14.6	11	0.04-0.59	0.17	1.4-57.5	4.5	63
MD-42B	8.4-13.3	10	0.05-1.05	0.14	1.4-124	3.7	73
Tico-2	3.4-337	5.7	0.43-23.9	1.17	4.1-915	11	5
ITQ-E	3.3-65.3	3.8	0.14-5.4	0.36	4.0-60.5	9.7	11
Cant-6	2.6-5.8	3.8	0.06-0.74	0.26	3.0-63.8	18	15
TAD-1	2.2-5.2	3.7	0.19-0.85	0.47	3.6-255	7.4	8

It is interesting to compare the behavior of P, an element that possibly enters the zircon structure in minor amounts, with Ca abundances. The diagram in Figure 35 shows a clear linear (positive) correlation, therefore suggesting that P contents in zircons may not be due entirely to P uptake in the zircon structure, but rather to the presence of tiny apatite (or even xenotime) inclusions in the analyzed zircon grains,

which may escape observation and are wrongly analyzed as zircon constituents. Alternative explanations are offered in the text, below, with the help of additional diagrams (cf. Figure 37, below).

Figure 35. Variation diagram for Ca and P abundances in the analyzed zircons.

8. DISCUSSION OF RESULTS

8.1. Ce and Eu anomalies as indicators of oxygen fugacities in magmas

The Ce and Eu anomalies determined in the REE diagrams in zircons give indications about the crystallization conditions of the analyzed zircon grains, as they serve to quantify the oxygen fugacities (Petke et al. 2005; Barth & Wooden 2010; Clairborne et al. 2010; Li et al. 2012).

The magnitude of the Eu anomaly depends on the fluid-magma oxidation state present at the time of the zircon crystallization (Trail et al. 2012). Bivalent Eu, a substitute for elements such as Ca and Sr, cannot be accommodated in the zircon structure, thus diminishing the total contents of the element in the host mineral. On the other hand, Ce^{3+} (ionic radius 1.143 Å) is the reduced equivalent of Ce^{4+} (ionic radius 0.970 Å), the last one better suited to replace in the zircon structure (or even

in other mineral phases) elements such as Zr, Hf and U (Hoskin & Schaltegger 2003; Trail et al. 2011, 2012).

The coexistence of the negative Eu and the positive Ce anomalies in the same zircon grains (Figure 32), far from representing an inconsistency, is perhaps better explained as representing the depletion of Eu, brought about by the fractionation in feldspars, host to Eu^{2+} , rather than representing a change in oxygen fugacity of the crystallizing magma (e.g., Hoskin & Schaltegger 2003).

Oxidizing conditions can be depicted in Eu/Eu^* and Ce/Ce^* diagrams (Figure 36; Orejana et al. 2011; Wang et al. 2013). In a Eu/Eu^* versus Ce/Ce^* plot, determinations in zircons indicate rather modest oxidizing conditions for most samples (formulae for Eu^* and Ce^* are $\text{Eu}^* = (\text{Sm}_N \times \text{Gd}_N)^{1/2}$ and $\text{Ce}^* = [(\text{La}_N)^{2/3} \times (\text{Nd}_N)^{1/3}]$).

A more or less well-defined linear relationship between Ce/Ce^* and Eu/Eu^* is observed especially in sample ITQ-E (Itaqui enclave), less so in grains from charnockite CHA-1. However, most determined results for the ratio Ce/Ce^* cluster around low values (e.g., less than 30 or even 10; Figure 36a), especially visible in samples Tico-2 (Tico-Tico), ITA-2 (Itaquera), IA-10D (Ilha Anchieta), Pe-04 (Perus), ITQ-2 (Itaqui granite), ITU-14X (Itu batholiths) Sr-07 (São Roque), TN-1 (Terra Nova), Cant-6 (Cantareira granite), TAD-1 (Taipas dike rock) and MD-42B (Cantareira “satellite”). CHA-1 (charnockite), as well as granitoids TAP-1 (main Taipas granite) and MD-24 (Itaqui “satellite”), show a wider scatter of Ce/Ce^* values (Figure 36a), possibly indicating that this ratio may be more sensitive to control by oxidizing conditions than the Eu/Eu^* ratio (Trail et al. 2012).

Coherent results were obtained for the Eu/Eu^* anomalies in zircons (Table 3), compared with those determined in the whole rock chemistry in samples ITA-2 (Itaquera), Tico-2, TN-1 (Terra Nova), Pe-04 (Perus) and ITU-14X (Table 1), this feature possibly controlled by plagioclase fractionation. The rock samples from Cantareira Cant 6, Cantareira “satellite” MD-42B, São Roque SR 07, Itaqui (ITQ-2, ITQ-E, MD-24), Taipas (TAP-1 and TAD-1) show no expressive Eu anomalies. In sample CHA-1 (charnockite), a well-defined Eu anomaly is observed in zircons (Figure 32), but not in the whole-rock pattern, where the lack of an anomaly may be controlled by an interplay between positive and negative contributions to that

anomaly from pyroxene and plagioclase (details on partition coefficients in Bea, 1996).

The core of one zircon grain in sample MD-24 (Itaqui “satellite”) presents an anomalous Ce/Ce* value of 184 and Eu/Eu* = 0.66 (cf. Table 3); its age of 3318 Ma (Janasi et al. 2015) is very different from the age determined in the outer zones, this sample clearly indicating that the core, representing a relict, crystallized (from magmas?) under different conditions than the outer zones.

Figure 36. Diagrams showing the possible oxidization state of magmas during zircon crystallization. **a)** Plot of Eu/Eu* versus Ce/Ce*. **b)** Plot of Ce/Ce* versus Hf (taken as a differentiation index) (source: El-Bialy & Ali, 2013).

Figure 36b presents an indication of possible oxidization state plotted against a differentiation index (abundance of Hf), again showing a narrow spread of values for both variables. These indices would indicate that the differentiation stage of these very different granites, as indicated by Hf abundances, is very similar for most analyzed samples; only a few samples are spread out along the Hf base line (Perus Pe-04, Tico-2 and Terra Nova TN-1). Zircon samples of ITQ-E (Itaqui enclave), CHA-1 (charnockite) and MD-24 (Itaqui “satellite”) are, again, distributed occupying a wider field than most other granites (cf. also Figure 36a). The spread of values (especially in the Itaqui enclave ITQ-E) may represent an indication of changes in oxygen fugacities and/or abundance of available water in the magma (e.g., El-Bialy & Ali, 2013), suggesting a control by different degrees of magma mixing, assuming that the

interpretation about the Itaqui enclave representing a magma mixing process is correct.

The zircon grains represented in the last two figures seem to have been formed by precipitation in a very narrow interval of oxygen fugacities and, possibly, also in a restricted time interval. Exceptions are zircons from samples CHA-1 (charnockite), and MD-24 (Itaqui “satellite”) covering a wider field of Ce/Ce* (varying from 20 to 80) and a narrow Hf content interval (from 10000 to 13000 ppm), possibly also indicating a smaller crystallization period.

8.2. Possible sources for LREE enrichment in zircons

LREE (La to Pr), presenting a larger ionic radius than the middle and heavy equivalents, are not easily introduced in the zircon structure as substitutions of Hf and Zr (Hoskin & Schaltegger 2003; Hanchar & van Westrenen 2007). On this account, La and Ce abundances in igneous zircon are of the order of ppm to sub-ppm; Ce may be found in contents up to 50 ppm. Our data, on the other hand, indicate for many zircon grains an enrichment factor for LREE of the order of 100 times the chondrite value, or even higher (Figure 37), for samples Cant 6 (Cantareira), ITQ-2 (Itaqui), TN-1 (Terra Nova), Pe-04 (Perus), ITU-14X (Itu batholith) and ITA-2 (Itaquera); the other samples show lower enrichment factors, less than 10^2 . The ratio $(\text{Sm/La})_N$, indicating the slope of the LREE, expected for crustal zircons are of the order of 57 to 547, much higher than the ones obtained from mantle zircons (11.3-38) (Hoskin & Schaltegger 2003).

The observation of high abundances of LREE in zircons, a topic discussed widely in the literature (Xia et al. 2010; Nardi et al. 2012; Orejana et al. 2012), will be addressed in the following lines. A possible explanation is of course that these values are fabricated by faulty analysis, in the sense that micro-inclusions of mineral phases hosting REE (apatites, monazites, etc.) were also included in the analytical procedure, a hypothesis that can be tested using chemical arguments, for instance by plotting $(\text{Sm/La})_N$ against P (Figure 38a), a plot that, however, shows no correlation and therefore is an argument for excluding an explanation based on undetected apatite inclusions (see also our discussion on the plot of P versus Ca abundances in zircons, above). Monazite inclusions, another source for higher LREE

abundances in zircons, would also be easily recognized by a plot of $(\text{Sm}/\text{La})_N$ against Th, the last element increasing given that possibility: no such feature is observed in the proper diagram (Figure 38b). LREE enrichment in apatites, in general, is only moderate, and somewhat higher in the MREE (Whitehouse & Kamber, 2002), igneous apatites however being strongly enriched in Sr, so that apatite inclusions in zircon could be recognized in plots of $(\text{Sm}/\text{La})_N$ versus Ca/Sr; no correlation is shown between the two factors in Figure 38c.

Figure 37. Contents of LREE in zircons. **a)** La_N versus Hf; **b)** Ce_N versus Hf; **c)** LREE_N versus Hf (values in ppm). Diagrams after Hoskin and Schaltegger (2003).

A general conclusion is that the higher LREE contents in the discussed zircons may represent a process directly related to their crystallization, certainly not dependent on foreign contributions (such as undetected phosphate inclusions).

On the other hand, hydrothermal “alteration” of zircons is a process that increases the amounts of LREE (Fu et al. 2009; Xia et al. 2010), a topic that will be discussed in a later section (cf. item 8.5, below). Experimental work on substitutions in zircons (Finch et al. 2001; Hancher et al. 2001) shows that a “xenotime” reaction could produce REE introduction into the zircon structure, such that $(\text{Y},\text{REE})^{3+} + \text{P}^{5+} = \text{Zr}^{4+} + \text{Si}^{4+}$. Limiting factors depend heavily on structural reasons (control of stresses on the Zr octahedron and Si tetrahedron in zircons generated with REE introduction).

Figure 38. Testing the hypothesis of microinclusions of apatite and other accessory minerals in zircon. (Sm/La)_N versus P, Th and Ca/Sr, respectively **a**), **b**), **c**). P and Th values in ppm. Diagrams after El-Bialy et Ali (2013) (cf. also Figure 35).

More complex chemical substitutions are discussed in Hoskin et al. (2000), showing that the relations P : REE can be related to an interplay with OH⁻ groups or O²⁺ anions and coupled reactions with Zr⁴⁺ (e.g., REE³⁺ + Nb⁵⁺ = 2 Zr⁴⁺). More complex xenotime-like substitutions can occur with REE, the ratios to P varying from 1:1 to 4:1 in zircons. These mechanisms may involve tetrahedrally bound Al³⁺, as well as charge balance being maintained by proper amounts of Li⁺ and Mg²⁺, Fe²⁺ and Fe³⁺, as seen in the following proposed reactions:

A plot of Y+REE versus P (atomic proportions) shows that all four possibilities can be taken into consideration as mechanisms affecting the incorporation of REE in the zircon structure (Figure 39). Other possibilities may, however, exist, as can be observed by the behavior of four zircon grains of TN-1 (Terra Nova), one of ITQ-E (Itaqui enclave), two from ITU-14X and SR-07 (São Roque), and all grains of TAD-1 (Taipas dike rock), that are either above the 4:1 line or below the 1:1 line, indicating that in these cases other mechanisms may be operating to compensate the introduction of REE (Figure 39).

Figure 39. Diagrams of Y+REE (atomic %) versus P (atomic %) found in the analyzed zircons, indicating the possibility for the existence of 1:1 to 1:4 reactions, as cited in text. Diagrams taken from Hoskin et al (2000).

8.3. Petrogenetic implications for the determined Th/U, Zr/Hf and U/Yb ratios

The Th/U ratios found in igneous zircons show usually values close to 0.5, or above (Hoskin & Schaltegger 2003), while metamorphic zircons present a very low value for the same ratio, not above ~ 0.1 (Rubatto 2002; Hoskin & Schaltegger

2003). Most of our values appear close to the cited ratio (Table 3). Values of 0.5 to 1 are found in samples CHA-1 (charnockite), TAP-1 and TAD-1 (Taipas main rock and dike), MD-24 (Itaqui “satellite”), IA-10D (Ilha Anchieta), SR-07 (São Roque), ITA-2 (Cantareira batholith) and ITQ-2 (Itaqui). Values for samples ITQ-E (Itaqui enclave), Tico-2 (Tico-Tico), Cant-6 and MD-42B (Cantareira batholith and “satellite”) and Pe-04 (Perus) vary between 0.1 to 0.5. A few samples (TN-1, Terra Nova; ITU-4X, Itu batholith) present values that are larger than 1 (cf. Figure 40).

Figure 40. Variation of the Th/U ratios in the analyzed zircons. Ratios Th/U of 1 (and down to 0.5) characterizes igneous zircons, while values of Th/U close to 0.1 are typical for metamorphic zircons (Hoskin & Schaltegger 2003).

Th and U concentrations in magmas are usually controlled by crystallization of monazite (Villaseca et al. 2003), Th being preferentially incorporated into this mineral by direct structural substitution of REE, leading to a high Th/U ratio (Hermann & Rubatto 2003). Orejana et al (2011) discuss the Th/U ratio in zircon and propose that Th can be made available to participate in zircon crystallization by the destruction or decomposition of monazite at higher magmatic temperatures. On the contrary, lower

Th/U ratios should be formed when zircon and monazite are crystallizing in apparent equilibrium or under conditions of lower temperature (metamorphism). Another possibility to elevate the Th/U ratio could occur by the co-precipitation of xenotime and titanite with zircon, the first two phases being important reservoirs of U in peraluminous and metaluminous granites (Bea, 1996) and competing for the uptake of the element, thereby reducing the availability of U in the residual magmas.

The mineral/melt partition coefficients for U and Yb in zircon (showing values such as 254 and 278, respectively; Bea et al, 1994; Grimes et al, 2007) indicate that they have nearly equivalent compatibility. Therefore, the U/Yb ratio for zircons should vary for different rock types in accordance with the availability of these elements in the melt, increasing from values found in oceanic gabbros (ratio 0.16) to those determined in continental granitoids (1.07) and kimberlites (2.1) (Grimes et al. 2007). Two diagrams (U/Yb versus Y and U/Yb versus Hf), as proposed by Grimes et al. (2007), discriminate between zircons formed in continental environments and those crystallized in oceanic areas. The entire set of our results plots within the field for continental zircons (Figure 41).

Figure 41. Diagrams showing variation of Hf (in ppm), and Y (in ppm) versus the U/Yb parameter for the analyzed zircon samples; diagrams according to Grimes et al (2007).

8.4. Ti geothermometry in zircons

Ti uptake in zircons is mainly controlled by environmental temperatures and Ti activity, a_{TiO_2} (Watson & Harrison 2005), making the concentration of the element a valuable tool for geothermometric studies (Watson & Harrison 2005; Watson et al. 2006; Ferry & Watson 2007). Calibration of this geothermometer (T_{zir}) was performed with the use of synthetic zircon for higher temperatures (1025 to 1450°C) and natural zircons for lower temperature conditions (560 to 1170°C; Watson et al. 2006). Diffusion of Ti^{4+} in zircons is a slow process, controlled by substitution of the element in the Si tetrahedron (Cherniak & Watson 2007; Ferry & Watson 2007). The substitution is most sensitive at pressures above 10 Kbar, making a correction of not more than 50°C necessary for crystallization conditions for crustal materials, formed at around 750°C (Ferry & Watson 2007).

The Ti geothermometer can best be applied to systems with pure TiO_2 and SiO_2 phases (that is, rutile and quartz), but can also be used in igneous rocks presenting ilmenite (Cates & Mojzsis 2009). It has been extensively applied in more recent studies (e.g., Clairborne et al. 2006; Fu et al. 2008; Orejana et al. 2011, 2012; Wang et al. 2013).

In our work, the geothermometer was applied according to calibrations performed by Watson & Harrison (2005) and Watson et al. (2006), under the assumption that crystallization proceeds, in the presence of quartz and rutile, at around 10 kbar; uncertainties in the obtained temperature estimates of zircon crystallization should not be over 60-70°C for environmental temperatures around 750°C (Ferry & Watson 2007).

Temperatures (T_{zir}) versus Hf diagrams are presented in Figure 42 for the analyzed zircon values. Zircon saturation temperatures in magmas ($T_{\text{sat Zr}}$) are indicated, calculated according to Watson & Harrison (1983), as well as apatite saturation temperatures ($T_{\text{sat Apt}}$), calculated according to Harrison & Watson (1984). Chemical data for these calculations were taken from Table 1 (geochemistry of rocks).

Samples CHA-1 (charnockite) and IA-10D (Ilha Anchieta) show the highest $T_{\text{sat Zr}}$ (zircon saturation; respectively 887°C and 855°C) and IA-10D the highest one for $T_{\text{sat Apt}}$ (apatite saturation; 1023°C). The high apatite solubility is related to the

high SiO_2 concentration (limit for use of the geothermometer is 75% SiO_2). Apatite saturation temperature for samples TAD-1 (Taipas dike) and TN-1 (Terra Nova) were not calculated, since their P_2O_5 values are below the detection limit for analytical determinations by means of XRF; besides, the SiO_2 percentage is above the limit of the geothermometric model.

Cant-6

MD-42B

TAP-1

TAD-1

ITQ-2

ITQ-E

MD-24

SR-07

ITA-2

Tico-2

ITU-14X

TN-1

CHA-1

IA-10D

Pe-04

Figure 42. Zircon crystallization temperatures (T_{zir}) in the studied granite samples, using the calibration by Watson et al. (2006), plotted against Hf as a differentiation index. The limit of Ti content in igneous unaltered zircon is also presented (according to Hoskin & Schaltegger 2003). Calculations of zircon and apatite saturation temperatures in magmas are listed as well (geothermometer by Watson & Harrison, 1983, and Watson, 1984).

Data in Figure 42 indicate that crystallization temperatures for zircons were below the temperatures, $T_{sat} \text{ Zr}$, calculated for the zircon saturation for samples CHA-1 (charnockite), IA-10D (Ilha Anchieta), TAP-1 (Taipas main rock) and ITA-2 (Itaquera). Well-formed zircon crystals with igneous zoning are observed in samples CHA-1 (charnockite), TAP-1 (Taipas main rock) and ITA-2 (Itaquera), presenting low contents of LREE. The TAD-1 sample presents three zircon grains with higher temperatures than the zircon saturation temperature $T_{sat} \text{ Zr}$, one of them even surpassing the temperature stated for an unaltered igneous zircon (996°C, Hoskin & Schaltegger 2003). This zircon grain apparently crystallized at 1137°C, with U and Th contents comparable to those determined in the other grains of the same sample, but with LREE abundances almost one order of magnitude higher than the other grains. Other zircon crystals with higher temperatures present contents of Th, U and REE that are compatible with the abundances found in grains crystallized at lower temperatures.

Sample ITQ-2 (Itaqui) shows a determined $T_{sat} \text{ Apt}$ (apatite saturation) of 1014°C, comparable to sample IA-10D (Ilha Anchieta), and $T_{sat} \text{ Zr}$ (zircon saturation) at 786°C. One zircon grain presents higher crystallization temperatures than the apatite saturation one, other grains lower temperature values; CL shows that the mentioned grain has a very dark core, suggesting that zircon crystallization began in very hot magmas, not saturated in apatite, probably crystallizing with elevated abundances of Th, U, Y and REE.

Grains in sample ITQ-E (Itaqui enclave) show Ti contents well below the detection limits, and one grain is observed with crystallization temperatures above the $T_{\text{sat Apt}}$ (apatite saturation), while other grains present temperatures between the calculated $T_{\text{sat Zr}}$ and $T_{\text{sat Apt}}$ (zircon saturation and apatite saturation). All these grains are very dark under CL, indicating high contents of U, Th, Y and REE (Hofmann et al, 2009).

Sample MD-24 (Itaqui “satellite”) presents zircon and apatite saturation temperatures comparable to the ones found in ITQ-2 (Itaqui main granite). Some grains show crystallization temperatures T_{zir} (804 and 922°C) between $T_{\text{sat Apt}}$ and $T_{\text{sat Zr}}$, the apatite saturation and zircon saturation temperatures, presenting contents of LREE somewhat higher, or mostly similar, to other analyzed points in several grains. One relictic grain (age of 3316 Ma; Janasi et al., 2015) presents temperatures of crystallization T_{zir} that do not differ from those of other grains, as well as normal Th and U abundances.

Sample Cant-6 (Cantareira main granite) shows several grains with crystallization temperatures between $T_{\text{sat Apt}}$ and $T_{\text{sat Zr}}$, the zircon and apatite saturation temperatures. Some grains yield T_{zir} crystallization temperatures of around 935°C, with core and oscillatory zoning behavior similar to that observed in most grains of the same sample, only differing by abundances of LREE (up to two orders of magnitudes higher). Sample MD-42B (Cantareira “satellite”) shows features that are similar to the ones found in Cant-6. One grain shows T_{zir} crystallization at 1024°C, with a dark core yielding an age of 2390 Ma (much higher than the probable margin crystallization age of 592 Ma; Janasi et al. 2015), presenting contents of LREE almost three order of magnitudes higher than other grains, although U and Th contents do not differ as much, compared to the rest. The possibility exists that these grains did crystallize in previous magmas (as suggested by the relictic character of the core) and are only partially showing the influence of the Cantareira magma chemistry.

The São Roque sample SR-07 shows two zircon grains with dark cores, with T_{zir} crystallization temperatures around 1004°C and 1035°C, higher than the $T_{\text{sat Apt}}$, apatite saturation temperatures (977°C), at the same being enriched in REE (especially the LREE), U, Th and Y; one crystal was dated at 2093 Ma, higher than the adopted age of the São Roque intrusion (603 Ma; Janasi et al. 2015).

The Tico-Tico sample (Tico-02) presents several grains with darker borders (CL), with crystallization temperatures of the order of 1300°C, much higher than $T_{\text{sat}}^{\text{Apt}}$, apatite saturation (942°C) and the accepted temperatures for granitic magmas; REE, Y, Th and U contents are usually much higher than those of other grains.

The ITU-14X sample presents several grains with a crystallization temperature of around 1000°C, above $T_{\text{sat}}^{\text{Apt}}$ (apatite saturation, 919°C). Again, these grains are enriched in REE, as well as in abundances of U, Th, Y, Ca and P.

Most zircons from sample TN-1 (Terra Nova) present T_{zir} crystallization temperatures well above those of $T_{\text{sat}}^{\text{Zr}}$, zircon saturation (770°C) and also over the expected unaltered igneous zircon temperatures (966°C, after Hoskin & Schaltegger 2003; cf. also Figure 42). The values of REE, Th, U, Y, Ca, P are well above those found in zircons from other samples (in this sample, apatite saturation values were not calculated, since the rock is high in silica and rather poor in P_2O_5).

Sample Pe-04 (Perus tourmaline granite) presents zircon grains with T_{zir} crystallization temperatures between 1189 and 1340°C, well above $T_{\text{sat}}^{\text{Apt}}$, apatite saturation values (905°C). These grains are extremely enriched in REE, as well as in Th, U, Y, Ca and P. Only the darker outer zones were analyzed, since the cores, usually very clear, are possibly other minerals (xenotime or intermediate xenotime-zircon phases (IXZP), Bea, 1996) showing mostly brilliant clear colors under CL and in backscattering images, presumably on account of light elements as Ca or a fluorescent effect related to phosphorus presence; previous analytical tests did show in the core of this grain higher Y_2O_3 (mean of 25%), P_2O_5 (11%), CaO (10%), ZrO_2 (24%), REE_T (10%) and SiO_2 (16%) abundances. These xenotime-IXZP type (foreign?) cores were later overgrown by true zircon border zones (Bea, 1996).

Another possibility is that temperature evaluations may reflect the larger uptake of amounts of Ti into the zircon structure, therefore conditioning the calculation of a higher “model” geothermometric temperature. Figure 43 presents a display of Ti contents as a function of total REE and P abundances within the analyzed zircons, plotted for those cases in which the $T_{\text{sat}}^{\text{Zir}}$ is lower than the calculated T_{zir} (compare with Figure 42), the abundances expressed as natural logarithms (presumably, providing an instrument to better visualize possible natural relationships). In most cases, a strong linear correlation (r over 0.80) is observed

between Ti and REE and a somewhat weaker one (r around 0.7 or less) for the relationships between Ti and P (Figure 43). The substitutions between those elements may be facilitated by the influence of fluid activities, as described in Speer (1980), Finch et al (2001) and Hoskin et al (2000), generating structural substitutions of Zr by REE^{3+} and charge equilibration by occupation of interstitial sites in zircons (Finch e Hanchar, 2003) by Fe^{3+} and Al^{3+} , compensating Si by P substitutions (Finch et al, 2001). Ionic radii of $^{\text{VI}}\text{Ti}^{3+}$ and $^{\text{VI}}\text{Ti}^{4+}$ are respectively 0.67 and 0.605 Å (Shannon, 1976), $^{\text{IV}}\text{Ce}^{4+}$ (a common REE in zircon) is 0.87 Å (Shannon, 1976). These ions may enter easily in the Zr site (ionic radius of $^{\text{VI}}\text{Zr}^{4+}$ equal to 0.72 Å), and possibly can also occupy of interstitial sites, in the last case competing with $^{\text{VI}}\text{Fe}^{3+}$ ($r=0.64$ Å, high spin radius). $^{\text{IV}}\text{Si}^{4+}$ presents ionic radius (0.26 Å) lower than $^{\text{IV}}\text{Ti}^{4+}$ (0.42 Å). Therefore, the positive correlation between those chemical variables (REE and Ti, and P and Ti; Figure 43) suggests that the calculated high “model” temperatures are a function of the high Ti abundances in zircons, produced by the presence of those foreign elements in the zircon structure, or facilitated by them.

Figure 43. Logarithmic relationships between REE and Ti (a) and P and Ti (b) for zircons from samples MD-42B, ITQ-2, ITQ-E, TAD-1, SR-07, Tico-2, TN-1, ITU-14X, Pe-04, and ITA-2, for the cases where the model T_{zir} is higher than the T_{satApt} (typically, $>1000^\circ\text{C}$).

Some authors suggest that the influx of hotter magmas, a cause for the determination of higher crystallization temperatures in zircons, is probably not registered by petrographic or field evidence, perhaps explaining in part the discrepancy in the estimates of the various geothermometers (e.g., Clairborne et al. 2010; Harrison et al. 2007; Barth & Wooden 2010).

Estimated Ti-in zircon model temperatures that are over 1000°C are caused by an increase in the Ti contents of the respective zircons, due to circumstances that are difficult to explain: they certainly do not correspond to “true” estimates of crystallizing granite magma temperatures. Our suggestion is that the Ti uptake in zircons may be controlled by late hydrothermal recrystallization processes (see data and discussion in the next topic).

8.5. Hydrothermal and late magmatic zircons

Most zircons in igneous rocks crystallized from magmas (mainly, those presenting a more evolved chemistry), but there are many situations in which these zircons are recrystallized varieties, or even formed entirely under non-magmatic conditions as, for instance, in those environments subjected to the activities of aqueous fluids at high temperature (e.g., Hoskin 2005; Cavosie et al. 2006; Fu et al. 2009; Bouvier et al. 2012; Lisowiec et al. 2013). Several paths for the generation of hydrothermal zircons have been proposed (Hoskin 2005):

1. Direct crystallization from aqueous fluids;
2. Ionic exchange between hydrothermal fluids and metamictic zircon of igneous origin;
3. Dissolution of earlier zircons and recrystallization, generating new zircons.

There is no consensus in the literature about the differences in composition between the truly igneous zircons and those formed under hydrothermal conditions, although several characteristics were pointed out for the second type, namely, an increase in contents of LREE, variations in abundances of HREE, and the possibilities of preservation or even formation of positive Ce/Ce* anomalies (Hoskin & Schaltegger 2003; Hoskin 2005; Pettke et al. 2005; Schaltegger 2007; Fu et al. 2009).

The diagram La_N versus Pr_N has been used by Hoskin & Schaltegger (2003) and Cavosie et al. (2006) to show clearly the different fields for hydrothermal and igneous zircons (Figure 44). In an extensive study by Yang et al. (2014), it was pointed out that zircons formed in the Chinese Baerzhe alkaline granite in the Central Asian Orogenic Belt, hosting one of the largest REE, Zr and Nb deposits, show a

rather porous structure, presenting frequently micro-inclusions of phases enriched in U, Th, Nb and Ta. These zircons were transformed by hydrothermal alteration forming phases characterized by an increase in ions easily transported in these solutions, such as U, Hf, Nb, Ta, Ti and LREE, the last ions - with larger sizes - being accommodated better in the structure under recrystallization than in the one offered by igneous zircons (e.g., Hachar & Westrenen 2007; Bakkar & Elburg 2006; Hay & Dempster 2009; van Lichtergerde et al. 2009).

The ion Zr itself is a rather mobile element in evolved peralkaline and peraluminous granitic systems, and also in hydrothermal environments enriched in F and silica (Rubin et al. 1993; Ayers et al. 2012). The solubility of Zr increases by formation of ionic complexes with silica and hydroxyl groups. At the same time, solubilities of several other elements are also increased, such as REE, Y, Nb, Hf, Pb, Th, U and Be, especially in hydrothermal fluids with relative abundances of fluorides and alkalis (Rubin et al. 1993).

Figure 44. Discriminator diagram La_N versus Pr_N showing different fields for hydrothermal and unaltered magmatic (igneous) zircons. After Hoskin & Schaltegger 2003; Cavosie et al. 2006.

Zircons with U and Th are of course easily damaged by the radioactive decay of these elements, forming frequently metamictic opaque grains with an amorphous

structure (e.g., Geisler et al. 2007), thus allowing penetration of later hydrothermal fluids and recrystallization, at the same time taking up several elements transported in those same hydrothermal fluids, also favoring a resetting of the isotopic clock (e.g., Hoskin et al. 2005; Erdmann et al. 2013; also Geisler et al. 2007; Martin et al. 2006).

Figure 45 presents diagrams showing the behavior of (REE+Y) vs (Nb + Ta + Mo) contents (abundances expressed as natural logarithms) in our studied zircons. A neat correlation is observed between the variables, especially for higher Nb + Ta values; Figure 45b focuses an area with high scatter of points, mainly restricted to those zircons grains with low REE and Nb and Ta values. On the other hand, Mo values show no correlation with either REE or Y abundances (figure not included).

Figure 46a shows a good positive correlation between (Y+REE) contents with those of (P+Ti+Ta+Nb) for all zircon grains presenting high Ti abundance, therefore yielding high “model” crystallization temperatures calculated with the T_{zir} geothermometer; the correlation coefficient ($r=0.88$) is high. Hydrothermal fluids may have incorporated the elements within the zircon structure in these grains, an incorporation facilitated by geometric reasons, given that $^{\text{VI}}\text{Nb}^{3+}$ and $^{\text{VI}}\text{Ta}^{3+}$ (with radius=0.64Å) can replace $^{\text{VI}}\text{Zr}^{4+}$ (radius= 0.72Å) or be accommodated in interstitial zircon sites. Increases in the calculated model geothermometric crystallization temperatures may be a result of such a behavior, whereby increases in the Ti abundances artificially produce higher temperatures, an argument that can be especially applied to those cases with calculated model temperatures showing values over 1000°C.

On the other hand, a good correlation is obtained ($r=0.83$) when P is plotted against (Y + REE) (Figure 46b), a xenotime substitution equilibrated by charge balance with the introduction of $^{\text{VI}}\text{P}^{5+}$ (radius= 0.38 Å) substituting more easily $^{\text{IV}}\text{Si}^{4+}$ (radius= 0.42Å), at the same time triggering an uptake of Y and REE.

Figure 45. The relationship between $\ln(\text{Nb} + \text{Ta} + \text{Mo})$ versus $\ln(\text{REE} + \text{Y})$ (all in ppm) in the studied samples. **Part b** of the figure is an enhanced version for the lower values of ($\text{Nb} + \text{Ta}$) (in **part a**). After Yang et al. (2014).

Figure 46. Logarithmic relationship between $(\text{REE} + \text{Y})$ versus $(\text{P} + \text{Ti} + \text{Nb} + \text{Ta})$ (**part a**), and $\text{REE} + \text{Y}$ versus P (**part b**).

Figure 47. Nb, Ta and Mo in the studied zircons samples. **Part a:** Nb versus Ta; **part b:** Nb versus Mo; **part c:** Ta versus Mo; **part d:** Nb versus Mo, a detail of part b. All values in ppm.

Mo and Nb values determined in zircons with no sign of hydrothermal alteration plot as two well defined clusters as functions of Nb and Mo abundances (Figure 47). The first cluster covers the values from 2 to 6 ppm Nb (versus 1 to 5 ppm Mo), encompassing samples ITQ-E (Itaqui enclave), Tico-2 (Tico-Tico), ITU-14X, and Cant 6 (Cantareira main granite), while the second one includes samples between 8 to 15 ppm Mo and 10 to 14 ppm Nb (samples MD-24, Itaqui “satellite”; IA-10D, Ilha Anchieta; MD-42B, Cantareira “satellite”; SR-07, São Roque; CHA-1, charnockite; TAP-1, Taipas main rock; ITQ-2, Itaqui main rock). If these values represent, to some extent, an inheritance from the original protolith, then the zircons with lower Mo, Nb and Ta values may be derived from rocks with residence time in the lower crust (estimated mean Mo, Nb and Ta values for the lower crust are, respectively 0.6, 5.0 and 0.6 ppm, in comparison with estimated mean values of 1.1, 12 and 0.9 ppm for the upper crust; cf. Rudnick & Gao, 2003).

A possible mechanism to explain mobility of heavy elements may point to a source related to mantle protoliths. Fluids generated in deeper regions (mantle domains) are supposed to be enriched in CO₂, H₂O, halides and certainly HFSE (e.g., Bea et al, 2001; Slaby et al, 2012; Lisowiec et al., 2013). Our studied recrystallized (“altered”) zircons are enriched in Nb, Ta and Y, also in some LILE (Rb, Ba, Sr), a situation pointing to activities related to mantle dynamics (e.g. Martin,

2006), in part also correlated with crustal dynamics (introduction of REE into the system; e.g., Bea, 1996). The history related to the strongly reworked crustal segments forming the Ribeira Belt creates conditions that may favor interaction between mantle sources and crustal domains (origin of heat increments, trigger mechanisms for fluid mobility), in parts heavily related to the activities developed as a result of fault dynamics, providing pathways for escape of fluids having deeper sources, as pointed out in the international literature (e.g., Pilli et al. 1997).

9. SUMMARY AND GENERAL CONCLUSIONS

Several different granites from various geologic domains identified in the basement areas of São Paulo state (domains São Roque, Embu, Jundiaí and Costeiro, according to Janasi & Ulbrich, 1992), all belonging to the so-called Brasiliano granite petrogenetic event, were sampled in order to perform a comparative study including litho-geochemistry, coupled with the information derived from trace-element geochemistry in zircons, to establish a framework to identify general petrogenetic crystallization conditions in those granites. The studied samples come from the following granite occurrences: Cantareira, Itaquí, São Roque and Itu calc-alkaline batholiths with some “satellite” bodies, Tico-Tico garnet-two mica granite, Perus tourmaline stocks, Taipas calc-alkaline bodies, Terra Nova occurrence, Itaquera two-mica granite, biotite granite from Ilha Anchieta (an island occurrence) and Ubatuba charnockite. Cantareira, Itaquí, Taipas, Perus, Tico-Tico and São Roque are positioned within the São Roque Domain, Itu and Terra Nova within the Itu Domain, Itaquera in the Embu area, and Ilha Anchieta and Ubatuba charnockite in the Costeiro (Coastal) Domain.

1. Whole-rock geochemistry of the analyzed granite samples indicates that they belong to meta-aluminous to peraluminous lineages with rather conspicuous K contents. The Cantareira (Cant-6) sample and a “satellite” body (MD-42B), as well as Taipas (TAP-1), Itaquí (ITQ-2 e 4), the Itaquí enclave (ITQ-E) and an Itaquí “satellite” (sampled at the Fazenda Itahyê. MD-24) and São Roque (SR-7) are meta-aluminous rocks, with high Sr abundances and a high Sr/Y ratio, presenting smooth normalized REE diagrams (no Eu anomaly is present): the parental magmas probably were

generated at higher depths and higher pressures (≥ 15 Kb), under conditions in which garnet is a stable phase in the protoliths, while plagioclase should be unstable. The other rocks show a geochemical profile compatible with rocks (or magmas) formed at lower crustal pressures, presenting a negative Eu/Eu* anomaly (produced by plagioclase interference, capturing bivalent Eu), and lower Sr contents, as well as a low Sr/Y ratio; included in this group are Itaquera samples (ITA-1, -2), some Itaqui rocks (ITQ-D1, a dike within the main granite), Tico-Tico (Tico-1 and -2), Terra Nova (TN-1), Itu batholith (ITU-14X), and Perus (Pe-04). The Itu sample within this group is the only meta-aluminous rock. The Taipas dike sample TAD-1 (occupying a dilatational fracture within the main Taipas granite) presents a positive Eu anomaly, low Sr contents and a higher Sr/Y ratio, features that characterize a residual liquid with complete feldspar crystallization as well as mineral phases that incorporate Y in their structure (e.g., garnets, monazite). The Ubatuba charnockite CHA-1 presents no Eu anomaly, indicating no influence of the plagioclase in the Eu distribution due to high quantities of clinopyroxene and hornblende in the rock. The charnockite shows features that point to a “primitive” (i.e., not evolved) character: for instance, the Eu/Sm ratio is similar to Bulk Crust (BC), a characteristic shared with Cantareira, Itaqui (including its enclave), São Roque and Taipas, showing however rather higher Rb and Eu contents and diminished Sr abundances than the four cited granite occurrences, possibly pointing to a higher contribution of sedimentary processes in the genesis of its protolith. Samples ITQ-E, ITQ-2 and -4, TAP-1, MD-24 (Itaqui “satellite”), SR-06, Cant-6 and MD-42B (Cantareira “satellite”) present Rb/Sr ratios comparable to the BC ratio (between 0.1 to 0.3), while in samples ITA-1 and -2, ITU-14X, Tico-1 and -2 and TN-1 the ratio increases a hundred times. This heavy increase in the ratio can be explained as the result of weathering processes that concentrate elements such as Rb in the weathering residue (especially in clays) and leached Sr at the same time, features that are, later on, transmitted into the recrystallized rocks that probably formed the protoliths of the corresponding magmas of the cited granitoids. An extreme example may be TN-1 (Terra Nova), showing values of 82 ppm Rb and 2.7 ppm Sr, indicating possibly that the protoliths of sedimentary origin concentrated Rb but lost heavily Sr during weathering processes.

2. The zircons extracted from these samples present, usually, rather high contents of REE, Th and U. The normalized variograms (spidergrams) of trace element contents in zircon from the analyzed samples present characteristic negative anomalies for Rb, Sr, P and Ti. On the other hand, normalized REE patterns show almost always a positive Ce anomaly and, for some samples, a negative one for Eu. The low Th/U ratios observed in some zircons are controlled by co-crystallization with monazite (samples Pe-04, ITA-2 and Tico-02), while dissolution of monazite in magmas liberates Th for uptake in zircons, therefore increasing their Th/U ratio in some samples (e.g., ITU-14X, TN-1) (cf. Orejana et al., 2011). Negative Rb and Sr anomalies in the spidergrams are to be expected in zircons, given possible incompatibilities for the incorporation of these elements in the zircon structure, as well as their uptake in the crystallizing feldspars.

3. Negative Eu anomalies ($\text{Eu}/\text{Eu}^* < 1$) are observed in samples Tico-2, Itu-14X (Itu main rock), TN-1 (Terra Nova), IA-10D (Ilha Anchieta), ITA-2 (Itaqui main rock), CHA-1 (charnockite) and Pe-04 (Perus tourmaline granite) and are determined by crystallization of zircon in equilibrium with plagioclase, which favors an uptake of Eu^{2+} in the feldspar structure. On the contrary, a positive Ce anomaly ($\text{Ce}/\text{Ce}^* > 1$) points to an increase in oxygen fugacities or, alternatively, a “wetter oxidized melt” (El-Bialy & Ali, 2013); the feature is best observed in samples CHA-1 (charnockite), TAP-1 and TAD-1 (Taipas main rock and dike), Itaqui “satellite” MD-24, Ilha Anchieta IA-10D, and Itaqui enclave ITQ-E.

4. A plot of the U/Yb ratio versus Hf, or U/Yb versus Y, clearly shows that our analyzed zircons crystallized in continental environments, as opposed to those generated during formation of an oceanic crust.

5. The observed high contents of REE (+ Y) in the analyzed zircons can be explained by uptake of the elements in those phases, given the possibility of coupled reactions occurring during zircon crystallization, with P^{5+} replacing Si^{4+} , and REE replacing Zr^{4+} , with the possible contribution of other elements, such as Al^{3+} , Fe^{3+} , Mg^{2+} , Fe^{2+} in interstitial sites, for charge balance. These coupled reactions would take the following expression: $(\text{Y, REE}) + \text{P} = \text{Zr} + \text{Si}$ (in a 1:1 REE:P

proportion, and similar reactions for 2:1, 3:1 and 4:1 proportions; see text, above). The other possibility, that of undetected micro-inclusions of phosphates analyzed within zircons, was discarded, since no correlation was observed between $(\text{Sm/La})_N$ versus P, or $(\text{Sm/La})_N$ versus Th (and other similar plots). This correlation would emerge if apatite and/or monazite were present as inclusions.

6. The calculation of the Ti-in-zircon model geothermometer T_{zir} (Watson & Harrison, 2005) in general yields estimated crystallization temperatures that are comparable to the ones obtained for the zircon and apatite saturation temperatures in magmas (respectively T_{satZir} and T_{satApt}), especially in the case of zircons showing a typical igneous texture, with well-formed cores and surrounding oscillatory idiomorphic rims. Zircon grains showing cores with an irregular outline, or signs of resorption (i.e., of a relictic nature), especially the ones with a dark reflection (under cathodoluminescence) yield crystallization temperatures above 1000°C, higher than to be expected for magmatic granitic rocks. Correlation plots of Ti versus REE and P contents within zircons showed a good positive correlation (coefficients over 0.80, for Ti versus REE, and 0.70, for Ti versus P). These features can be explained as a result of incorporation of these elements in the zircon structure, by means of Zr substitution by Ti and REE, with correlated charge balance by introduction of P in the Si site (and, eventually, other elements such as Fe, Al, Mg in interstitial positions); Ti may also enter the structure occupying some interstitial positions, in addition to the Zr site.

7. Plots of Nb, Ta and Mo against REE + Y, as well as those of P + Ti + Ta + Nb against REE + Y, based on the studies of Hoskin et al. (2005) and Erdman et al. (2013), show a clear correlation, suggesting recrystallization of zircons under the influence of fluid activities (hydrothermal conditions, as opposed to typical igneous crystallization from magmas). These correlations point to the importance of transport of these elements in fluids and the possibility of incorporating them into zircons, a situation that may also apply to explain the introduction of U and Th by a similar transport mechanism. It is known that these fluids, transporting HFSE, are also enriched in halides (chlorides and fluorides), as well as alkalis, silica and CO₂, thus

providing for a favorable chemical environment which may also help in the capture and transport of HFSE (Dubrill et al. 2011; Lisowiec et al. 2013).

8. It is difficult, and certainly speculative, to indicate a possible source from which the HFSE, later introduced into zircons, were taken and mobilized, but literature discussions can point towards certain possibilities, the mantle being foremost among them. Mantle-generated fluids are supposed to be enriched in CO₂, H₂O, halides and HFSE (Bea et al, 2001; Slaby et al, 2012). Our “altered” zircons present high abundances of Nb, Ta and Y, as well as of Rb, Ba, Sr (LILE), pointing to contributions derived from mantle activities (Martin, 2006), to which contributions inherited from crustal sources (the REE) are also added. The general geological framework shown by the Ribeira Belt rocks, with their protracted history of deformation and recrystallization, magma generation and shear-zone fault activities, should also indicate the possibility of parallel extensive fluid activities (the “hidden” part of geologic history). There is no way to deny the importance of fluid activities during diagenetic processes shaping the final texture and mineralogy of sedimentary rocks: fluids would certainly also plays a major role in the long-lasting formation history of basement rocks. In a way, the recognition of “altered” zircons, clearly showing that the trace-element geochemistry contained in typical igneous zircons can be changed rather drastically, is a further indication that fluids play a major role overprinting existing zircons. Avenues for fluid transport are certainly present, both as metamorphic structures (foliations, etc.) as well as major faults, such as the ever-present shear-fracture zones in the studied basement areas.

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ELETRONIC SUPPLEMENTARY TABLES

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS.

(%)	ITA-01	ITA-02	TAP-01	TAD-01	Pe-04	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Tico-1
SiO₂	73.71	73.61	68.47	74.59	74.30	67.61	65.81	51.18	73.57	64.68	73.55
TiO₂	0.175	0.173	0.601	0.027	0.077	0.787	0.759	1.627	0.040	0.882	0.13
Al₂O₃	13.55	13.64	15.18	13.55	14.44	13.33	14.72	15.87	14.25	14.96	13.75
Fe₂O₃ (tot.)	1.60	1.59	2.84	0.45	1.23	4.85	4.67	10.40	0.18	4.99	1.82
MnO	0.034	0.033	0.049	0.012	0.029	0.081	0.080	0.197	0.004	0.092	0.088
MgO	0.12	0.12	0.80	< 0.01	0.06	1.85	1.65	4.52	< 0.01	1.70	0.06
CaO	1.10	1.11	2.51	0.79	0.77	3.79	3.65	7.42	0.84	3.45	0.66
Na₂O	3.15	3.15	3.88	3.32	3.81	3.47	3.51	3.93	4.63	3.38	3.23
K₂O	5.23	5.22	4.30	6.14	3.91	2.91	4.13	3.04	4.88	4.26	5.16
P₂O₅	0.041	0.041	0.207	<0.001	0.070	0.347	0.284	0.676	0.049	0.379	0.115
Loss on Ignition	0.48	0.42	0.57	0.31	0.47	0.60	0.57	0.85	0.79	0.92	0.70
Σ Total	99.19	99.11	99.41	99.19	99.17	99.63	99.83	99.71	99.23	99.69	99.27
FeO(tot.)	1.44	1.43	2.56	0.41	1.11	4.37	4.20	9.36	0.16	4.49	1.64
FeO/(FeO+MgO)	0.92	0.92	0.76	1.00	0.95	0.70	0.72	0.67	1.00	0.73	0.96
Na ₂ O+K ₂ O	8.38	8.37	8.18	9.46	7.72	6.38	7.64	6.97	9.51	7.64	8.39
A/CNK (IAS _T)	1.05	1.06	0.97	1.00	1.21	0.84	0.87	0.68	0.99	0.91	1.13
A/NK (IAS _P)	1.25	1.26	1.37	1.12	1.37	1.50	1.43	1.62	1.10	1.47	1.26
T _{sat.} zirc. (°C)	776	776	786	668	697	786	781	701	683	790	744
T _{sat.} Apt (°C)	857	856	967	n.d.	905	1014	978	908	872	963	953

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

(ppm)	ITA-01	ITA-02	TAP-01	TAD-01	Pe-04	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Tico-1
Ba	469	461	1110	58	17	625	1200	597	55	1354	66
Ce	116	140	78.6	3.41	53.1	103	112	118	17.9	106	33
Co	< 6	< 6	6	< 6	< 6	11	9	27	< 6	9	< 6
Cr	15	14	< 13	<13	< 13	37	35	22	< 13	17	15
Cs	9.24	9.04	8.15	2.29	6.61	2.08	2.30	2.59	6.13	1.13	3.10
Cu	< 5	< 5	< 5	< 5	< 5	7	15	117	< 5	9	< 5
Dy	4.53	4.55	1.90	0.06	7.35	2.84	2.72	4.75	3.53	3.80	5.89
Er	2.68	2.40	0.78	0.04	3.83	1.23	1.20	2.14	1.67	1.75	2.86
Eu	0.63	0.64	1.45	0.07	0.16	1.79	1.75	2.96	0.23	2.06	0.25
F	1186	1003	1283	< 500	< 500	1051	1042	1739	< 500	775	1561
Ga	21	19	21	24	20	18	18	24	21	18	23
Gd	4.69	5.08	3.36	0.09	6.63	4.70	4.61	7.78	3.39	6.60	3.89
Hf	4.78	4.62	5.99	2.23	1.72	5.42	5.31	5.37	1.81	6.27	2.89
Ho	0.98	0.94	0.35	0.01	1.45	0.53	0.51	0.90	0.68	0.67	1.20
La	58.4	70.8	39.6	2.04	23.2	52.6	59.9	50.0	8.46	53.3	16.5
Lu	0.42	0.37	0.10	0.02	0.55	0.17	0.17	0.30	0.22	0.18	0.31
Mo	1.37	1.74	1.63	< 0.01	< 0.01	1.37	0.86	0.75	0.19	n.d.	2.25
Nb	19.7	20.7	11.0	1.62	4.25	14.3	13.7	18.9	19.8	n.d.	23.9
Nb	19.9	23.8	10.3	0.45	4.0	15.2	16.9	20.7	23.3	17.4	18.0
Nd	38.1	44.6	29.9	1.05	20.3	40.8	40.1	55.0	7.80	44.7	13.3
Ni	5	6	5	< 5	< 5	12	13	11	< 5	9	< 5
Pb	38.6	38.3	29.1	66.0	49.0	18.4	23.0	17.5	77.7	23.1	24.6
Pr	12.0	14.2	8.28	0.32	5.69	11.3	11.3	14.1	2.07	11.9	3.85
Rb	298	290	141	170	245	100	118	117	242	115	217

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

(ppm)	ITA-01	ITA-02	TAP-01	TAD-01	Pe-04	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Tico-1
Sc	3.00	2.74	3.86	1.96	3.65	7.07	5.45	19.4	2.57		2.80
Sm	6.79	7.58	5.20	0.14	6.58	7.09	6.79	10.4	2.82	7.89	3.64
Sn	6.40	6.10	1.45	0.22	3.43	1.83	1.88	3.36	2.12	n.d.	8.70
Sr	116	117	641	92	28	763	861	795	58	810	32
Ta	2.15	2.28	0.65	0.08	0.87	1.08	1.03	1.20	3.14	n.d.	1.95
Tb	0.78	0.83	0.41	0.01	1.30	0.59	0.57	0.97	0.64	0.77	0.92
Th	25.2	24.7	8.6	11.4	14.1	10.8	13.0	8.22	5.52	10.9	8.67
Tm	0.43	0.37	0.11	0.01	0.61	0.18	0.18	0.31	0.24	0.23	0.41
U	4.87	6.92	1.57	6.35	8.15	2.50	3.01	1.93	18.7	2.75	5.18
V	< 9	16	49	9	< 9	82	73	231	< 9	72	< 9
Y	27.3	25.0	8.73	0.53	46.3	15.5	15.0	26.5	20.5	20.0	36.3
Yb	2.79	2.45	0.67	0.08	3.85	1.14	1.10	1.92	1.49	1.26	2.50
Zn	36	36	57	10	47	73	67	141	2	75	31
Zr	137	136	187	36	42	230	217	214	45	233	84
Ba/Sr	4.1	3.9	1.7	0.6	0.6	0.8	1.4	0.8	1.0	1.7	2.1
Sr/Y	4.2	4.7	73.4	175.4	0.6	49.2	57.5	29.9	2.8	40.4	0.9
Rb/Sr	2.58	2.48	0.22	1.85	8.92	0.13	0.14	0.15	4.19	0.14	6.13
Rb/Ba	0.64	0.63	0.13	2.94	14.69	0.16	0.10	0.20	4.40	0.08	3.30
Σ REE	249	295	171	7	135	228	243	269	51	241	89
(La/Lu)N	14.6	19.8	39.3	10.0	4.4	31.3	37.0	17.6	4.1	30.1	5.4
(La/Sm)N	5.4	5.9	4.8	9.1	2.2	4.7	5.6	3.0	1.9	4.3	2.8
Eu/Eu*	0.34	0.32	1.06	1.83	0.08	0.95	0.95	1.01	0.22	0.87	0.21

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

(%)	Tico-2	SR-07	TN-1	Cant-6	MD-42B	ITU-14X	CHA-01	IA-10
SiO₂	73.97	64.46	78.66	68.54	72.28	73.80	64.80	64.24
TiO₂	0.123	0.864	0.104	0.581	0.449	0.379	0.699	0.99
Al₂O₃	13.83	14.49	11.49	14.73	13.63	12.62	15.11	14.64
Fe₂O₃ (tot.)	1.59	5.07	0.95	3.13	1.99	2.16	5.61	5.43
MnO	0.076	0.080	0.063	0.065	0.039	0.065	0.095	0.11
MgO	0.05	1.72	< 0.01	0.69	0.50	0.29	0.52	1.11
CaO	1.02	3.27	0.35	2.13	1.91	0.99	2.68	2.87
Na₂O	3.08	3.04	3.91	3.72	3.84	3.52	3.75	3.33
K₂O	4.81	4.79	4.38	5.02	4.07	5.35	5.28	4.85
P₂O₅	0.099	0.318	0.030	0.199	0.141	0.088	0.219	0.34
Loss on ignition	0.75	1.88	0.24	0.80	0.68	0.41	0.10	0.87
Σ Total	99.39	99.98	100.18	99.60	99.53	99.68	98.86	98.78
FeO(tot.)	1.43	4.56	0.86	2.81	1.79	1.94	5.05	4.89
FeO/(FeO+MgO)	0.97	0.73	1.00	0.80	0.78	0.87	0.91	0.81
Na ₂ O+K ₂ O	7.89	7.83	8.29	8.74	7.91	8.87	9.03	8.18
A/CNK (IAS _T)	1.14	0.90	0.97	0.95	0.96	0.94	0.90	0.92
A/NK (IAS _P)	1.34	1.42	1.03	1.27	1.27	1.09	1.27	1.36
T _{sat.} zirc. (°C)	736	790	770	787	778	837	887	855
T _{sat.} Apt (°C)	942	977	843	964	1002	919	935	1023

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

(ppm)	Tico-2	SR-07	TN-1	Cant-6	MD-42B	ITU-14X	CHA-01	IA-10
Ba	75.2	1335	6.10	1481	688	877	1347	1385
Ce	30.9	120	44.4	71.5	58.1	118	118	n.d.
Co	< 6	10	< 6	< 6	< 6	< 6	< 6	8
Cr	18	20	24	22	< 13	14	< 13	< 13
Cs	4.19	1.80	1.95	2.01	2.28	2.02	0.42	n.d.
Cu	< 5	9	< 5	7	< 5	6	6	< 5
Dy	4.27	3.87	4.73	1.45	1.39	4.86	8.03	n.d.
Er	2.19	1.72	2.35	0.53	0.50	2.96	4.44	n.d.
Eu	0.28	2.01	0.47	1.22	1.04	1.12	3.44	n.d.
F	2111	746	< 500	1437	< 500	1882	< 500	2239
Ga	21	20	13	22	20	16	20	22
Gd	3.16	6.73	5.49	2.97	2.98	5.45	9.89	n.d.
Hf	3.27	6.18	4.32	4.29	4.29	6.57	14.8	n.d.
Ho	0.88	0.67	0.98	0.25	0.20	1.10	1.71	n.d.
La	15.8	60.0	20.0	41.2	29.0	68.8	54.9	n.d.
Lu	0.28	0.21	0.26	0.06	0.06	0.48	0.65	n.d.
Mo	2.01	n.d.	1.55	1.46	n.d.	2.36	1.51	n.d.
Nb	24.7	n.d.	15.9	8.34	n.d.	37.5	23.2	n.d.
Nb	25.4	22.6	12.3	8.66	10.1	36.4	28.6	n.d.
Nd	12.3	48.4	23.3	29.4	22.5	44.0	54.8	n.d.
Ni	< 5	11	7	< 5	< 5	< 5	< 5	< 5
Pb	27.8	26.1	15.9	25.9	35.6	21.5	20.3	n.d.
Pr	3.56	13.2	5.97	7.96	6.28	12.9	13.9	n.d.
Rb	255	133	92	140	138	201	111	180

legend: n.d. - not determined

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

(ppm)	Tico-2	SR-07	TN-1	Cant-6	MD-42B	ITU-14X	CHA-01	IA-10
Sc	3.10	n.d.	1.44	2.65	n.d.	3.39	11.1	n.d.
Sm	3.16	8.37	6.46	4.72	3.64	7.36	11.4	n.d.
Sn	8.02	n.d.	2.43	1.56	n.d.	5.07	0.87	n.d.
Sr	34.2	713	2.67	664	426	155	166	315
Ta	2.42	n.d.	1.40	0.47	n.d.	2.83	1.07	n.d.
Tb	0.68	0.78	0.87	0.34	0.32	0.85	1.45	n.d.
Th	7.61	14.8	6.43	10.1	8.11	33.2	7.26	n.d.
Tm	0.33	0.23	0.33	0.07	0.06	0.46	0.65	n.d.
U	5.32	3.20	1.17	2.51	2.81	7.27	1.07	4.00
V	6	85	3	43	35	14	23	58
Y	25.5	18.8	24.6	6.64	5.77	29.0	45.4	69.0
Yb	2.14	1.40	2.03	0.43	0.37	3.23	4.11	
Zn	39	74	34	63.00	50	42	87	99
Zr	96.0	235	131	194	162	247	646	553
Ba/Sr	2.2	1.9	2.3	2.2	1.6	5.7	8.1	4.4
Sr/Y	1.3	37.9	0.1	100.0	73.8	5.3	3.6	4.6
Rb/Sr	7.32	0.19	30.6	0.19	0.33	1.15	0.67	0.57
Rb/Ba	3.39	0.10	15.07	0.09	0.20	0.23	0.08	0.13
Σ REE	80	267	118	162	126	272	288	
(La/Lu) _N	5.9	29.3	7.9	69.0	53.4	14.8	8.8	
(La/Sm) _N	3.1	4.5	1.9	5.5	5.0	5.9	3.0	
Eu/Eu*	0.27	0.82	0.24	0.99	0.96	0.54	0.99	

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

CIPW Norm	ITA-01	ITA-02	TAP-01	TAD-01	Pe-04	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Tico-1
Qz	32.065	31.973	22.181	30.113	35.622	26.42	20.22		26.27	19.74	33.85
Or	30.935	30.876	25.434	36.317	23.127	17.21	24.43	17.981	28.86	25.20	30.52
Plg: ab	26.623	26.623	32.792	28.059	32.201	29.33	29.67	31.948	39.13	28.57	27.30
Plg: an	5.193	5.243	11.111	3.885	3.366	12.17	12.17	16.641	3.65	13.02	2.53
C	0.787	0.870	0.054		2.694						1.910
Di: wo				0.015		1.830	1.711	6.587	0.086	0.683	
Di: en						1.185	1.121	3.847	0.000	0.496	
Di: fs						0.518	0.467	2.418	0.097	0.123	
Wo											
Hi: en	0.300	0.300	2.000		0.150	3.440	3.004			3.754	0.150
Hi: fs	1.987	2.006	2.850		0.084	1.503	1.252		0.137	0.931	
Ol: fo								5.217			
Ol: fa								3.621			
Ap	0.095	0.095	0.480		0.162	0.804	0.658	1.566	0.114	0.878	0.266
Ilm	0.333	0.329	1.142	0.051	0.146	1.495	1.442	3.091	0.076	1.676	0.247
Mt	0.250	0.230	0.548	0.371	1.097	2.832	2.861	4.534	0.000	3.454	0.462
Hem				0.053							1.312
Tit											
Fr											
Ne								0.687			

Table 1. Whole-rock geochemical data and normative data (CIPW) for the studied granitoids. Major and trace elements in boldface were obtained by FRX; others trace elements by ICPMS (*continuação*).

CIPW Norm	Tico-2	SR-07	TN-1	Cant-6	MD-42B	ITU-14X	CHA-01	IA-10
Qz	35.71	19.74	38.63	22.83	30.22	30.90	15.17	17.47
Or	28.45	28.33	25.91	29.66	24.07	31.64	31.23	26.20
Plg: ab	26.03	25.69	33.05	31.44	32.45	29.75	31.69	31.69
Plg: an	4.29	11.70	0.83	8.63	7.30	2.79	8.75	9.99
C	1.970				0.219			
Di: wo		1.029	0.323	0.268		0.611	1.304	1.584
Di: en		0.727		0.231	1.250	0.000	0.276	1.073
Di: fs		0.211					1.119	0.386
Wo								
Hi: en	0.125	0.727		1.494		0.725	1.024	2.727
Hi: fs		0.211					4.158	0.982
Ol: fo								
Ol: fa								
Ap	0.229	0.737	0.007	0.461	0.327	0.204	0.507	1.066
Ilm	0.163	1.642	0.135	1.104	0.161	0.673	1.328	1.881
Mt	0.000	3.428		1.555			1.759	3.611
Hem	1.623		1.604	1.008	1.949	1.879		
Tit	0.092		0.081		0.892	0.061		
Fr								0.460
Ne								

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

CANTAREIRA (Cant-6)							
Isotope (ppm)	cant-6_1 <i>grey rim</i>	cant-6_16 <i>grey rim</i>	cant-6_3 <i>grey rim</i>	cant-6_4 <i>grey rim</i>	cant-6_13 <i>grey rim</i>	cant-6_12 <i>grey rim</i>	cant-6_8 <i>grey rim</i>
⁷ Li	16.3	8.54	<1.53	7.64	5.10	<1.86	3.61
²⁴ Mg	30.1	<0.99	1.89	<0.95	65.6	2.98	<1.08
²⁷ Al	481	<2.53	11.1	10.8	617	84.8	49.5
²⁹ Si	175357	162746	132288	182866	161400	129345	164625
³¹ P	111	<38.81	47.8	<32	143	98	135
⁴⁴ Ca	<303	<280	303	<246	<339	344	<331
⁴⁵ Sc	360	316	319	343	347	274	390
⁴⁹ Ti	63.8	<3.00	3.65	<3.00	63.0	24.7	9.66
⁵⁵ Mn	19.1	<1.08	0.86	<0.97	12.8	4.62	2.35
⁵⁶ Fe	3592	<39	<44	<52	1452	491	570
⁸⁵ Rb	1.67	<0.20	0.33	<0.21	0.41	0.19	0.29
⁸⁸ Sr	5.18	0.49	0.56	0.13	2.68	1.30	0.48
⁸⁹ Y	689	354	362	106	841	784	595
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	3.65	3.35	3.9	2.61	3.96	4.25	3.33
⁹⁵ Mo	3.06	3.04	0.91	2.61	4.13	3.38	4.18
¹³⁷ Ba	7.60	<0.43	<0.22	<0.30	3.81	1.01	<0.49
¹³⁹ La	32.9	0.07	0.14	0.37	19.5	5.86	3.55
¹⁴⁰ Ce	284	21.1	14.3	9.7	214	94.4	50.7
¹⁴¹ Pr	52.7	0.07	0.14	0.55	36.1	11.3	6.61
¹⁴³ Nd	335	0.88	1.90	4.44	226	78.7	42.3
¹⁴⁷ Sm	175	1.01	1.88	2.08	137	43.2	27.1
¹⁵¹ Eu	46.5	0.89	0.78	0.79	35.1	13.6	8.91
¹⁵⁷ Gd	161	6.15	7.42	2.35	122	61.4	35.9
¹⁵⁹ Tb	23.3	2.05	2.13	0.64	23.0	13.4	6.68
¹⁶³ Dy	126	24.7	22.4	7.0	132	96.6	53.0
¹⁶⁵ Ho	23.1	9.2	9.1	2.3	27.9	23.8	18.0
¹⁶⁶ Er	70.1	47.6	48.6	11.2	94.4	83.0	78.7
¹⁶⁹ Tm	12.5	10.5	12.4	2.96	17.1	14.6	17.1
¹⁷³ Yb	117	116	124	36	149	124	186
¹⁷⁵ Lu	25.0	29.2	33.0	8.18	32.2	28.9	46.7
¹⁷⁹ Hf	12916	11319	12598	13358	12347	10617	13200
¹⁸¹ Ta	0.12	0.15	0.32	0.06	0.09	0.26	0.26
²⁰⁷ Pb	14.8	9.91	8.45	7.34	11.4	4.36	11.3
²⁰⁸ Pb	13.8	12.7	9.14	3.39	13.6	9.43	11.2
²³² Th	303	190	144	56	304	201	218
²³⁸ U	903	383	370	202	489	277	469
<i>T_{zirc}</i> (°C)	935		660		934	827	738

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

CANTAREIRA (Cant-6)

Isotope (ppm)	cant-6_1 <i>grey rim</i>	cant-6_16 <i>grey rim</i>	cant-6_3 <i>grey rim</i>	cant-6_4 <i>grey rim</i>	cant-6_13 <i>grey rim</i>	cant-6_12 <i>grey rim</i>	cant-6_8 <i>grey rim</i>
Th / U	0.34	0.50	0.39	0.28	0.62	0.73	0.47
U / Yb	7.7	3.3	3.0	5.6	3.3	2.2	2.5
Zr / Hf	38	44	39	37	40	47	38
La _N	139	0.3	0.6	1.6	82	25	15
Ce _N	464	35	23	16	349	154	83
Pr _N	555	0.7	1.5	5.8	380	119	70
LREE _N	1158	36	26	23	812	298	167
Sm _N	1141	7	12	14	893	282	177
(Sm / La) _N	8.2	22	20	8.7	11	11	12
Nd _N	717	1.9	4.1	10	484	168	91
Gd _N	785	30	36	11	594	299	175
Eu _N	802	15	13	14	606	235	154
Ce _N / Ce*	1.9	63	21	5.5	2.4	3.3	3.0
Eu _N / Eu*	0.8	1.1	0.6	1.1	0.8	0.8	0.9
Yb / Ta	998	767	389	626	1658	488	705
Y / Nb	189	106	93	41	212	184	179
Σ REE	1483	269	279	89	1265	693	581
Y+ Σ REE	2173	623	641	195	2106	1477	1176

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

CANTAREIRA (Cant-6)								
Isotope (ppm)	cant-6_9 <i>grey rim</i>	cant-6_11 <i>grey rim</i>	cant-6_14 <i>grey rim</i>	cant-6_15 <i>white core</i>	cant-6_2 <i>white core</i>	Median	Mean	sd
⁷ Li	<1.89	7.03	2.86	2.36	1.70	5.10	6.13	3.34
²⁴ Mg	3.13	<1.12	6.73	10.7	<0.83	6.73	17.3	17.4
²⁷ Al	82.8	31.1	281	15	10.6	49.5	152	168
²⁹ Si	158316	154792	156529	164006	140464	159858	156895	11843
³¹ P	37.6	<47	214	259	195	135	138	58
⁴⁴ Ca	<232	<347	<387	339	<213	340	329	17
⁴⁵ Sc	409	396	318	273	275	331	335	39
⁴⁹ Ti	24.5	5.59	30.4	10.5	4.06	17.5	24.0	17.3
⁵⁵ Mn	6.07	<1.32	3.53	<1.2	1.25	4.08	6.32	4.81
⁵⁶ Fe	467	<50	<53	264	<50	531	1139	922
⁸⁵ Rb	<0.19	<0.26	0.47	0.34	<0.18	0.34	0.53	0.33
⁸⁸ Sr	0.92	1.27	0.62	0.48	0.37	0.59	1.21	0.93
⁸⁹ Y	557	832	743	998	1794	716	721	277
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	
⁹³ Nb	3.65	5.13	3.93	3.66	5.76	3.78	3.93	0.56
⁹⁵ Mo	4.74	2.33	3.88	3.30	3.74	3.34	3.28	0.74
¹³⁷ Ba	0.37	<0.69	1.37	<0.41	<0.30	1.37	2.83	2.30
¹³⁹ La	5.43	3.64	4.77	0.17	0.46	3.60	6.41	6.60
¹⁴⁰ Ce	66.0	70.3	86.7	27.3	102	68.2	86.7	57.9
¹⁴¹ Pr	9.26	4.94	13.5	0.38	1.50	5.78	11.4	11.3
¹⁴³ Nd	65.6	28.0	95.3	4.58	17.5	35.2	75.0	72.5
¹⁴⁷ Sm	34.0	12.6	51.0	7.35	20.8	24.0	42.7	39.1
¹⁵¹ Eu	10.6	6.27	13.2	4.20	11.1	9.76	12.7	9.63
¹⁵⁷ Gd	43.0	24.2	58.7	31.4	85.3	39.5	53.3	37.1
¹⁵⁹ Tb	7.46	5.64	11.2	9.42	22.5	8.44	10.6	6.70
¹⁶³ Dy	52.3	69.6	76.6	99.6	194	73.1	79.4	41.7
¹⁶⁵ Ho	16.3	24.1	22.0	34.2	55.0	22.5	22.1	9.2
¹⁶⁶ Er	68.1	109	87.7	139	198	80.9	86.3	32.8
¹⁶⁹ Tm	15.4	22.9	18.1	29.2	33.0	16.2	17.1	5.8
¹⁷³ Yb	159	217	175	250	275	154	161	50
¹⁷⁵ Lu	45.7	49.9	39.7	52.6	49.4	36.3	36.7	10.6
¹⁷⁹ Hf	12996	11264	11036	9870	10038	11833	11796	1106
¹⁸¹ Ta	0.20	0.41	0.36	0.40	0.74	0.26	0.28	0.14
²⁰⁷ Pb	8.91	11.9	8.67	2.92	8.53	8.79	9.04	2.35
²⁰⁸ Pb	7.46	16.1	10.3	7.3	21.2	10.7	11.3	3.5
²³² Th	173	262	137	124	398	196	209	73
²³⁸ U	461	498	434	109	396	415	416	127
<i>T_{zirc}</i> (°C)	827	692	849	745	667	786	787	87

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

CANTAREIRA (Cant-6)

Isotope (ppm)	cant-6_9 <i>grey rim</i>	cant-6_11 <i>grey rim</i>	cant-6_14 <i>grey rim</i>	cant-6_15 <i>white core</i>	cant-6_2 <i>white core</i>	Median	Mean	sd
Th / U	0.38	0.53	0.31	1.13	1.00	0.48	0.6	0.2
U / Yb	2.9	2.3	2.5	0.4	1.4	2.71	3.1	1.2
Zr / Hf	38	44	45	50	49	42.0	43	4.0
La _N	23	15	20	0.7	1.9	15.2	27	28
Ce _N	108	115	142	45	166	111	142	95
Pr _N	97	52	142	4.0	16	60.8	120	119
LREE _N	228	182	304	49	184	183	289	236
Sm _N	222	83	333	48	136	157	279	256
(Sm / La) _N	10	5.4	17	67	70	11.6	22	16
Nd _N	140	60	204	10	37	75.3	161	155
Gd _N	209	118	285	153	415	192	259	180
Eu _N	183	108	227	72	192	168	218	166
Ce _N / Ce*	2.6	4.8	3.3	26	32	4.0	14	14
Eu _N / Eu*	0.8	1.1	0.7	0.8	0.8	0.8	0.9	0.1
Yb / Ta	785	530	489	621	371	624	702	234
Y / Nb	153	162	189	273	311	181	174	53
Σ REE	598	648	753	690	1065	669	701	294
Y + Σ REE	1155	1480	1496	1688	2858	1478	1422	554

Q.L. = Quantitation Limit

D.L. = Detection Limit

sd= standard deviation

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Cantareira Satellite (MD-42B)									
Isotope (ppm)	pto26 rim	pto27 rim	pto13-1 rim	pto12 rim	pto15 rim	pto16 rim	pto22 rim	pto18 rim	pto2 core
⁷ Li	1.76	2.54	1.18	1.51	<1.13	8.86	1.24	1.77	<4.19
²⁴ Mg	1.00	12.7	<0.43	<0.39	0.77	0.78	1.28	<0.61	6.19
²⁷ Al	3.18	140	4.81	5.1	6.03	4.68	5.45	<2.13	76.5
²⁹ Si	153547	183126	180853	170899	169970	175921	173661	179090	190474
³¹ P	68.1	<187	47.3	102	<59	<75	89	<50	516
⁴⁴ Ca	<248	<1160	<269	<282	<366	<463	<384	<310	1501
⁴⁵ Sc	353	401	426	340	323	266	305	355	464
⁴⁹ Ti	1.54	7.48	3.70	2.35	3.05	<2.50	3.65	1.43	9.39
⁵⁵ Mn	<1.3	<6.2	<1.4	<1.4	<1.9	<2.4	<1.9	1.89	<7.2
⁵⁶ Fe	21.7	180	18.4	<10	32.5	<16	88.9	19.0	<48
⁸⁵ Rb	<0.08	<0.38	<0.10	0.17	<0.10	<0.12	0.15	0.09	<0.49
⁸⁸ Sr	0.23	1.09	0.78	0.52	0.42	0.39	0.39	0.30	0.52
⁸⁹ Y	396	315	316	321	378	208	557	297	391
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	10.2	10.7	8.35	10.0	10.4	10.2	10.4	9.96	13.3
⁹⁵ Mo	11.2	10.3	8.70	10.9	12.1	5.72	10.0	10.5	13.9
¹³⁷ Ba	0.19	<1.0	<0.23	<0.11	<0.14	<0.44	<0.15	<0.17	0.91
¹³⁹ La	0.10	2.55	0.46	0.40	0.37	1.09	0.13	0.22	4.36
¹⁴⁰ Ce	20.0	31.6	16.8	13.4	15.6	38.9	20.0	12.2	56.3
¹⁴¹ Pr	0.33	3.08	1.16	0.13	0.30	0.96	0.40	0.12	6.60
¹⁴³ Nd	2.46	25.6	8.73	1.01	2.91	5.71	3.25	0.56	45.0
¹⁴⁷ Sm	2.41	12.3	3.76	1.06	2.24	2.22	3.08	1.63	17.5
¹⁵¹ Eu	1.10	3.39	1.70	0.69	1.32	1.10	1.80	1.05	5.02
¹⁵⁷ Gd	7.53	14.4	7.41	6.26	8.36	6.27	13.2	7.16	18.2
¹⁵⁹ Tb	2.41	2.45	2.08	1.70	2.52	1.89	4.39	2.41	4.98
¹⁶³ Dy	22.1	23.5	24.3	23.4	29.2	14.4	46.0	22.7	30.0
¹⁶⁵ Ho	8.78	7.42	9.46	8.58	11.3	6.00	15.9	8.51	10.3
¹⁶⁶ Er	43.5	35.5	43.8	41.7	47.6	22.7	71.1	40.6	52.3
¹⁶⁹ Tm	9.63	7.60	9.87	9.29	10.5	4.53	13.9	8.89	11.4
¹⁷³ Yb	108	92.9	99.0	94.9	111	58.8	139	95.8	139
¹⁷⁵ Lu	27.7	21.6	29.1	24.6	28.3	12.6	32.8	24.6	34.2
¹⁷⁹ Hf	11199	11562	13308	12313	11789	12811	10714	11768	13464
¹⁸¹ Ta	0.21	<0.08	0.053	0.08	0.092	0.164	0.331	0.077	<0.07
²⁰⁷ Pb	7.33	6.75	9.16	4.27	5.53	14.6	4.31	4.29	3.72
²⁰⁸ Pb	8.3	5.06	9.79	5.15	5.99	18.1	5.07	4.36	8.27
²³² Th	143	94.5	97.5	87.4	90.8	206	80.7	219	153
²³⁸ U	380	359	328	192	202	333	164	211	301
T_{zirc}(°C)	599	716	661	628	646		660	595	735

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Cantareira Satellite (MD-42B)

(ppm)	pto26 rim	pto27 rim	pto13-1 rim	pto12 rim	pto15 rim	pto16 rim	pto22 rim	pto18 rim	pto2 core
Th / U	0.38	0.26	0.30	0.46	0.45	0.62	0.49	1.04	0.51
U / Yb	3.5	3.9	3.3	2.0	1.8	5.7	1.2	2.2	2.2
Zr / Hf	44	43	37	40	42	39	46	42	37
La _N	0.4	10.8	1.9	1.7	1.6	4.6	0.5	0.9	18.4
Ce _N	33	52	27	22	26	63	33	20	92
Pr _N	3.5	32	12	1.3	3.1	10	4.2	1.3	69
LREE _N	37	95	42	25	30	78	37	22	180
Sm _N	16	80	25	6.9	15	15	20	11	114
(Sm / La) _N	38	7.4	13	4.1	9.3	3.2	37	11	6.2
Nd _N	5.3	55	19	2.2	6.2	12	7.0	1.2	96
Gd _N	37	70	36	30	41	31	64	35	88
Eu _N	19	58	29	12	23	19	31	18	87
Ce _N / Ce*	34	2.8	6.7	12	10	10	26	20	2.9
Eu _N / Eu*	0.8	0.8	1.0	0.8	0.9	0.9	0.9	0.9	0.9
Yb / Ta	512		1868	1186	1209	359	419	1244	
Y / Nb	39	29	38	32	36	21	54	30	29
Σ REE	256	284	258	227	272	177	365	226	435
Y + Σ REE	652	598	573	548	649	386	921	523	826

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Cantareira Satellite (MD-42B)						
Isotope (ppm)	pto4 core	pto7-1 core	pto28 core	Median	Mean	sd
⁷ Li	4.17	9.66	0.73	1.77	3.34	2.53
²⁴ Mg	48.8	242	<0.50	3.74	39.1	53.0
²⁷ Al	338	2900	33.7	6.03	320	473
²⁹ Si	186623	197741	151005	177505	176076	10242
³¹ P	<150	404	225	102	207	149
⁴⁴ Ca	<941.04	845	783.22	845	1043	306
⁴⁵ Sc	367	407	341	354	362	42
⁴⁹ Ti	18.6	124	2.12	3.65	16.1	20.0
⁵⁵ Mn	<5.0	24.7	1.92	1.92	9.50	10.1
⁵⁶ Fe	90.8	1645	23.7	32.5	236	313
⁸⁵ Rb	0.20	8.70	<0.08	0.17	1.86	2.74
⁸⁸ Sr	0.36	3.57	1.02	0.47	0.80	0.55
⁸⁹ Y	413	843	496	384	411	111
⁹¹ Zr	496007	496007	496007	496007	496007	
⁹³ Nb	9.73	13.3	9.90	10.2	10.5	0.9
⁹⁵ Mo	12.1	9.25	10.7	10.6	10.4	1.4
¹³⁷ Ba	<0.82	10.9	0.20	0.56	3.04	3.91
¹³⁹ La	0.61	48.7	1.84	0.54	5.07	7.26
¹⁴⁰ Ce	22.4	384	29.9	21.2	55.1	55.0
¹⁴¹ Pr	1.50	57.8	0.66	0.81	6.08	8.70
¹⁴³ Nd	8.94	355	4.54	5.13	38.7	53.8
¹⁴⁷ Sm	5.23	119	3.31	3.20	14.4	17.9
¹⁵¹ Eu	3.27	44.5	1.40	1.55	5.53	6.49
¹⁵⁷ Gd	11.3	76.4	14.4	9.83	15.9	10.5
¹⁵⁹ Tb	3.42	10.1	4.16	2.49	3.54	1.58
¹⁶³ Dy	31.8	75.2	44.2	26.7	32.2	11.5
¹⁶⁵ Ho	12.9	24.0	15.0	9.89	11.51	3.62
¹⁶⁶ Er	56.4	113	60.8	45.7	52.4	15.2
¹⁶⁹ Tm	13.3	25.3	13.1	10.2	11.4	3.3
¹⁷³ Yb	137	268	120	110	122	32
¹⁷⁵ Lu	31.5	52.5	30.7	28.7	29.2	6.0
¹⁷⁹ Hf	11192	10767	12335	11779	11935	759
¹⁸¹ Ta	0.12	1.05	0.27	0.14	0.24	0.18
²⁰⁷ Pb	5.58	63.1	6.09	5.84	11.23	9.21
²⁰⁸ Pb	6.44	44.6	8.37	7.36	10.79	6.85
²³² Th	110	125	162	118	131	38
²³⁸ U	311	423	241	306	287	71
<i>T_{zirc}</i> (°C)	799	1024	621	660	698	87

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Cantareira Satellite (MD-42B)

Isotope (ppm)	pto4 core	pto7-1 core	pto28 core	Median	Mean	sd
Th / U	0.35	0.30	0.67	0.45	0.49	0.15
U / Yb	2.3	1.6	2.0	2.2	2.6	1.0
Zr / Hf	44	46	40	42	42	3
La _N	2.6	205	8	2	21	31
Ce _N	37	628	49	35	90	90
Pr _N	16	608	6.9	9	64	92
LREE _N	55	1441	64	48	175	212
Sm _N	34	776	22	21	94	117
(Sm / La) _N	13	3.8	2.8	8.4	12.5	8.6
Nd _N	19	761	10	11	83	115
Gd _N	55	372	70	48	77	51
Eu _N	56	767	24	27	95	112
Ce _N / Ce*	7.3	2.0	5.8	8.6	11.6	7.5
Eu _N / Eu*	1.3	1.4	0.6	0.9	0.9	0.2
Yb / Ta	1180	255	450	846	868	469
Y / Nb	42	64	50	37	39	9
Σ REE	339	1653	344	278	403	214
Y+ Σ REE	752	2496	840	650	814	305

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Taipas (TAP-01)								
Isotope (ppm)	pto9 white rim	pto13 grey rim	pto12 grey rim	pto1 grey rim	pto2 grey rim	pto3 white rim	pto5 white rim	pto6 black rim
⁷ Li	2.55	<1.18	1.20	2.91	<0.78	<1.43	1.33	5.69
²⁴ Mg	0.78	<0.42	0.32	<0.49	<0.34	<0.63	<0.45	5.14
²⁷ Al	218	23.7	<2.7	2.77	<3.2	3.46	15.8	17.1
²⁹ Si	179035	184697	196811	175771	186233	170164	173632	170506
³¹ P	<68	93.5	<69	<54	<74	108	98.5	175
⁴⁴ Ca	<377	<369	<391	<300	<423	<379	<385	438
⁴⁵ Sc	251	323	354	365	293	259	294	311
⁴⁹ Ti	3.76	4.96	2.94	11.26	2.36	3.6	3.55	2.89
⁵⁵ Mn	<2.19	<2.2	2.35	<1.8	<2.5	<2.1	<2.2	<2.1
⁵⁶ Fe	<14	19.8	42.5	<12	<17	18.1	<14	<14
⁸⁵ Rb	1.16	0.18	<0.12	0.13	0.18	0.13	0.24	0.18
⁸⁸ Sr	0.88	0.78	0.36	0.30	0.29	0.25	0.51	0.75
⁸⁹ Y	530	929	517	459	353	534	809	569
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	11.5	12.7	11.3	10.1	11.0	11.0	12.4	12.2
⁹⁵ Mo	10.8	10.4	11.3	11.1	11.9	12.7	10.8	12.1
¹³⁷ Ba	0.41	0.93	<0.28	0.31	<0.18	<0.28	0.39	0.49
¹³⁹ La	<0.04	0.122	<0.02	0.034	<0.04	0.047	0.105	0.268
¹⁴⁰ Ce	17.1	41.7	17.3	12.0	15.0	18.4	30.7	22.0
¹⁴¹ Pr	0.06	0.11	0.13	0.07	0.04	0.11	0.11	0.16
¹⁴³ Nd	0.83	2.64	1.90	1.36	1.72	1.00	2.14	2.04
¹⁴⁷ Sm	2.53	3.96	2.74	2.69	1.92	3.02	3.82	2.01
¹⁵¹ Eu	1.01	2.1	1.47	1.11	1.52	1.53	2.44	1.44
¹⁵⁷ Gd	10.4	21.7	13.1	9.98	7.97	15.3	19.0	13.4
¹⁵⁹ Tb	3.88	7.26	3.96	3.53	2.83	4.88	6.87	4.18
¹⁶³ Dy	43.4	82.5	39.3	36.0	29.5	47.3	70.2	45.6
¹⁶⁵ Ho	16.0	28.7	14.3	12.6	10.1	16.6	25.5	17.0
¹⁶⁶ Er	74.6	120.2	66.0	59.4	45.5	71.6	110.3	74.5
¹⁶⁹ Tm	15.7	24.5	14.1	12.5	9.63	13.9	22.7	16.5
¹⁷³ Yb	153	230	151	137	99.5	133	214	165
¹⁷⁵ Lu	31.6	47.9	34.9	33.1	23.7	27.1	46.4	36.5
¹⁷⁹ Hf	11856	11212	11775	13000	12191	11337	11329	11862
¹⁸¹ Ta	0.52	0.46	0.26	0.17	0.24	0.25	0.46	0.39
²⁰⁷ Pb	3.20	4.24	3.12	4.65	3.87	3.38	4.75	6.90
²⁰⁸ Pb	3.29	8.62	5.01	6.16	3.32	4.56	8.67	11.31
²³² Th	61.5	144	96.3	133	60.4	65.3	153	206
²³⁸ U	135	189	155	253	115	114	192	310
<i>T_{zirc}</i>(°C)	662	683	644	752	628	658	657	642

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Taipás (TAP-01)

Isotope (ppm)	pto9 white rim	pto13 grey rim	pto12 grey rim	pto1 grey rim	pto2 grey rim	pto3 white rim	pto5 white rim	pto6 black rim
Th / U	0.46	0.76	0.62	0.53	0.52	0.57	0.80	0.66
U / Yb	0.9	0.8	1.0	1.8	1.2	0.9	0.9	1.9
Zr / Hf	42	44	42	38	41	44	44	42
La _N		0.51		0.14		0.20	0.44	1.13
Ce _N	28	68	28	20	25	30	50	36
Pr _N	0.6	1.2	1.3	0.7	0.4	1.1	1.1	1.7
LREE _N	28	70	30	20	25	31	52	39
Sm _N	17	26	18	18	13	20	25	13
(Sm / La) _N		50		123		100	56	12
Nd _N	1.8	5.7	4.1	2.9	3.7	2.1	4.6	4.4
Gd _N	50	106	64	49	39	74	93	65
Eu _N	17	36	25	19	26	26	42	25
Ce _N / Ce*		60		50		69	52	20
Eu _N / Eu*	0.60	0.69	0.75	0.65	1.19	0.69	0.88	0.85
Yb / Ta	294	505	577	805	416	532	466	419
Y / Nb	46	73	46	46	32	49	65	47
Σ REE	370	613	360	321	249	353	554	400
Y+ Σ REE	901	1542	877	780	602	887	1364	969

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Taipas (TAP-01)							
Isotope (ppm)	pto16 white rim	pto15 white core	pto17 rim-core	pto18 black rim-core	Median	Mean	sd
⁷ Li	2.88	<0.93	<1.08	5.47	2.88	3.15	1.39
²⁴ Mg	<0.49	0.87	<0.67	0.69	0.78	1.56	1.43
²⁷ Al	<2.7	<2.7	<2.7	2.57	15.8	40.5	50.7
²⁹ Si	174946	184460	181659	184755	180347	180222	6213
³¹ P	158	<63	97.2	<57	103	122	30
⁴⁴ Ca	<359	<358	<368	<333	438	438	0.0
⁴⁵ Sc	247	363	278	285	293	302	34
⁴⁹ Ti	<2.21	3.86	5.11	3.48	3.60	4.34	1.51
⁵⁵ Mn	<2.02	<2.03	<2.07	<1.88	2.35	2.35	0.00
⁵⁶ Fe	<14	<13	39.6	36.6	36.6	31.3	9.89
⁸⁵ Rb	<0.14	0.20	0.13	<0.10	0.18	0.28	0.20
⁸⁸ Sr	0.65	0.31	0.31	0.38	0.37	0.48	0.19
⁸⁹ Y	533	342	710	219	532	542	141
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	10.8	10.7	11.7	10.0	11.1	11.3	0.7
⁹⁵ Mo	10.3	11.3	10.6	13.8	11.2	11.4	0.8
¹³⁷ Ba	<0.143	<0.26	<0.26	<0.19	0.41	0.51	0.17
¹³⁹ La	0.253	<0.03	<0.03	0.1	0.11	0.13	0.07
¹⁴⁰ Ce	15.7	11.1	24.2	11.7	17.2	19.7	6.61
¹⁴¹ Pr	0.11	<0.03	0.10	0.06	0.11	0.09	0.03
¹⁴³ Nd	1.31	0.83	1.26	1.21	1.34	1.52	0.47
¹⁴⁷ Sm	2.29	0.81	3.30	1.29	2.61	2.53	0.72
¹⁵¹ Eu	1.37	0.66	1.74	0.54	1.46	1.41	0.39
¹⁵⁷ Gd	11.6	6.17	16.9	3.39	12.4	12.4	4.16
¹⁵⁹ Tb	4.40	1.95	5.75	1.20	4.07	4.22	1.34
¹⁶³ Dy	46.0	24.4	59.4	12.4	44.5	44.7	13.8
¹⁶⁵ Ho	16.7	10.1	20.5	5.11	16.3	16.1	4.7
¹⁶⁶ Er	76.5	49.2	89.9	26.1	73.1	72.0	19.0
¹⁶⁹ Tm	15.6	11.8	18.4	6.21	14.8	15.1	3.8
¹⁷³ Yb	146	135	170	65.1	148	150	31
¹⁷⁵ Lu	30.7	32.0	35.5	18.7	32.5	33.2	5.9
¹⁷⁹ Hf	11664	13468	10948	11581	11719	11852	520
¹⁸¹ Ta	0.39	0.13	0.39	0.13	0.32	0.32	0.12
²⁰⁷ Pb	2.67	4.29	3.31	3.90	3.89	4.02	0.79
²⁰⁸ Pb	2.90	3.42	7.08	5.36	5.19	5.81	2.13
²³² Th	53.6	48.7	82.7	87.6	85.1	99.4	39.9
²³⁸ U	110	134	138	151	145	166	46.5
<i>T_{zirc}</i>(°C)		664	685	656	658	666	21.8

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Taipas (TAP-01)

(ppm)	pto16 white rim	pto15 white core	pto17 rim-core	pto18 black rim-core	Median	Mean	sd
Th / U	0.49	0.36	0.60	0.58	0.6	0.6	0.1
U / Yb	0.8	1.0	0.8	2.3	0.9	1.2	0.4
Zr / Hf	43	37	45	43	42	42	1.8
La _N	1.07			0.42	0.4	0.6	0.3
Ce _N	26	18	40	19	28	32	10.8
Pr _N	1.1		1.1	0.6	1.1	1.0	0.3
LREE _N	28	18	41	20	29	33	11.2
Sm _N	15	5.3	22	8.4	17	17	4.7
(Sm / La) _N	14			20	50	53	33.7
Nd _N	2.8	1.8	2.7	2.6	2.9	3.3	1.0
Gd _N	56	30	82	16	60	60	20.2
Eu _N	24	11	30	9.3	25	24	6.8
Ce _N / Ce*	17			25	50	42	18.0
Eu _N / Eu*	0.81	0.90	0.71	0.79	0.8	0.8	0.1
Yb / Ta	375	1038	433	516	485	531	138
Y / Nb	50	32	61	22	46	47	10
Σ REE	368	284	447	153	364	373	87
Y+ Σ REE	901	626	1157	372	894	915	229

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Fazenda Itahy� (MD-24)								
Isotope (ppm)	pto 15 <i>rim</i>	pto 14 <i>rim</i>	pto 19 <i>rim</i>	pto 22 <i>rim</i>	pto 16 <i>rim</i>	pto 8.1 <i>rim</i>	pto 1 <i>rim</i>	pto 11 <i>rim</i>
⁷ Li	2.28	<0.86	1.69	2.21	<0.52	<1.65	6.27	<0.64
²⁴ Mg	0.42	0.57	<0.63	1.96	0.57	4.52	0.94	<0.60
²⁷ Al	<2.90	5.93	7.87	<2.93	<2.00	13.9	<2.96	<3.01
²⁹ Si	184691	180831	173505	159572	168689	161677	159153	172093
³¹ P	<59	<64	<84	<60	<45	111	91.3	104
⁴⁴ Ca	<267.49	<289	<403	<296	<218	<455	<326	<332
⁴⁵ Sc	272	263	279	240	269	263	250	277
⁴⁹ Ti	2.95	2.63	5.38	7.25	4.54	2.98	<1.96	4.42
⁵⁵ Mn	<1.72	<1.86	<2.56	<1.86	<1.39	<2.93	<2.12	<2.10
⁵⁶ Fe	21.5	<19	53.8	<18	<14	<28	<20	48.0
⁸⁵ Rb	0.16	<0.103	0.287	0.194	<0.068	0.186	<0.122	<0.115
⁸⁸ Sr	0.56	0.26	0.37	0.25	0.32	0.33	0.30	0.51
⁸⁹ Y	505	424	727	430	458	482	316	654
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	10.1	9.10	10.7	10.1	10.2	11.8	10.8	9.93
⁹⁵ Mo	9.22	9.79	11.5	8.43	9.53	13.9	13.0	10.6
¹³⁷ Ba	<0.25	<0.28	<0.30	<0.21	0.34	<0.34	<0.20	<0.24
¹³⁹ La	0.22	0.03	0.16	0.08	0.12	0.15	0.21	0.36
¹⁴⁰ Ce	33.2	18.7	30.7	25.7	17.1	20.9	19.4	23.4
¹⁴¹ Pr	0.13	0.04	0.25	0.21	0.12	0.15	0.33	0.25
¹⁴³ Nd	1.76	0.60	3.25	1.24	1.99	2.1	1.65	3.54
¹⁴⁷ Sm	2.35	0.90	3.42	1.27	2.13	1.53	1.85	3.69
¹⁵¹ Eu	1.33	0.89	1.89	1.00	1.32	0.69	0.65	1.76
¹⁵⁷ Gd	10.5	7.8	14.5	8.18	7.36	6.53	4.53	15.9
¹⁵⁹ Tb	3.34	2.32	4.76	2.56	2.09	2.56	1.38	4.69
¹⁶³ Dy	36.1	27.0	54.1	28.5	29.4	29.1	18.9	49.3
¹⁶⁵ Ho	14.1	11.3	20.3	11.0	11.5	13.1	7.84	18.8
¹⁶⁶ Er	67.9	59.8	102	53.0	59.3	68.8	42.6	91.6
¹⁶⁹ Tm	14.8	14.0	22.4	12.6	14.5	16.6	11.2	20.7
¹⁷³ Yb	154	167	251	138	162	187	132	224
¹⁷⁵ Lu	35.1	40.4	58.0	32.1	39.2	45.6	31.7	53.8
¹⁷⁹ Hf	10294	10343	11796	9932	10131	9887	11482	10920
¹⁸¹ Ta	0.27	0.19	0.17	0.16	0.15	0.17	0.17	0.12
²⁰⁷ Pb	5.42	4.27	5.11	4.56	2.72	3.94	5.35	4.65
²⁰⁸ Pb	12.1	5.32	9.42	9.97	4.86	6.37	6.92	7.58
²³² Th	207	92	170	164	92	100	123	150
²³⁸ U	231	159	218	215	159	179	224	179
<i>T_{zirc}</i> (�C)	644	636	689	713	676	645		674

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Fazenda Itahy (MD-24)

	pto 15	pto 14	pto 19	pto 22	pto 16	pto 8.1	pto 1	pto 11
	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>
Th / U	0.90	0.58	0.78	0.76	0.58	0.56	0.55	0.84
U / Yb	1.5	1.0	0.9	1.6	1.0	1.0	1.7	0.8
Zr / Hf	48	48	42	50	49	50	43	45
La _N	0.9	0.1	0.7	0.3	0.5	0.6	0.9	1.5
Ce _N	54	30	50	42	28	34	32	38
Pr _N	1.4	0.4	2.6	2.2	1.2	1.6	3.5	2.6
LREE _N	56	31	53	44	30	36	36	42
Sm _N	15	5.9	22	8.3	14	10	12	24
(Sm / La) _N	17	45	33	25	27	16	14	16
Nd _N	3.8	1.3	7.0	2.7	4.3	4.5	3.5	7.6
Gd _N	51	38	71	40	36	32	22	77
Eu _N	23	15	33	17	23	12	11	30
Ce _N / Ce*	37	109	34	63	27	28	23	15
Eu _N / Eu*	0.8	1.0	0.8	0.9	1.0	0.7	0.7	0.7
Yb / Ta	567	860	1442	876	1081	1128	779	1869
Y / Nb	50	47	68	42	45	41	29	66
Σ REE	375	350	567	316	348	395	274	512
Y + Σ REE	880	775	1293	745	807	877	590	1165

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Fazenda Itahyé (MD-24)									
Isotope (ppm)	pto 31 <i>rim</i>	pto 32 <i>rim</i>	pto 33 <i>rim</i>	pto 36 <i>rim</i>	pto 40 <i>rim</i>	pto 37 <i>rim</i>	pto 17 <i>rim</i>	pto 38 <i>rim-core</i>	pto 8.1n <i>white core</i>
⁷ Li	6.72	5.4	3.28	<1.34	3.96	1.94	<1.02	<1.95	<1.01
²⁴ Mg	46.7	1.35	0.59	2.39	<0.47	2.44	<0.53	1.37	<0.59
²⁷ Al	94.8	<3.15	4.52	15.3	5.94	6.55	113	24.5	<3.02
²⁹ Si	186598	178366	175880	186441	175426	143985	169834	166769	164837
³¹ P	<85	105	<99	<71	71.5	199	74.6	<119	<64
⁴⁴ Ca							<316		<330
⁴⁵ Sc	245	255	235	272	283	285	323	302	269
⁴⁹ Ti	4.99	3.37	3.6	<2.58	<2.42	6.43	4.39	19.64	<2.28
⁵⁵ Mn	3.57	<2.20	<2.73	<2.12	<1.93	<1.58	<2.00	5.02	<2.08
⁵⁶ Fe	77.42	<16	<19	<15	39	12.4	46.4	<25	<20
⁸⁵ Rb							0.5		<0.104
⁸⁸ Sr	0.32	0.58	0.62	0.33	0.36	1.33	1.05	0.60	0.32
⁸⁹ Y	390	505	528	535	650	721	464	809	537
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	10.4	10.8	11.9	10.1	12.1	13.1	11.0	12.3	10.4
⁹⁵ Mo	12.2	10.3	13.3	11.1	11.9	12.9	10.7	12.5	11.3
¹³⁷ Ba	0.44	<0.33	<0.40	<0.39	<0.32	<0.259	2.48	1.02	<0.20
¹³⁹ La	<0.032	0.39	0.18	0.16	0.03	2.51	0.81	4.51	0.08
¹⁴⁰ Ce	28.6	34.2	30.3	25.5	39.7	53.3	22.2	63.1	20.1
¹⁴¹ Pr	<0.047	0.16	0.09	0.26	0.14	0.93	1.11	5.30	0.09
¹⁴³ Nd	1.06	1.46	0.74	2.10	1.28	2.75	5.67	32.13	1.23
¹⁴⁷ Sm	1.34	1.84	1.87	2.96	2.26	2.38	3.24	14.48	1.88
¹⁵¹ Eu	0.86	1.29	1.72	1.66	0.97	1.44	1.95	6.06	1.19
¹⁵⁷ Gd	8.27	9.09	12.0	13.7	10.4	12.5	8.02	29.4	9.96
¹⁵⁹ Tb	2.49	3.10	3.52	4.31	3.68	4.6	2.18	6.12	3.21
¹⁶³ Dy	29.2	36.7	42.1	44.3	40.4	58.1	22.4	65.9	34.4
¹⁶⁵ Ho	11.5	15.0	16.6	16.5	17.3	22.1	10.9	27.6	14.9
¹⁶⁶ Er	53.7	69.9	78.7	80.9	88.7	108	57.8	123	70.5
¹⁶⁹ Tm	13.0	16.6	18.4	18.3	19.5	24.0	14.4	26.4	16.3
¹⁷³ Yb	149	184	212	204	221	283	180	298	177
¹⁷⁵ Lu	34.9	42.7	50.8	46.9	51.8	62.6	48.2	72.6	44.1
¹⁷⁹ Hf	10954	10903	11552	11495	10084	10575	12057	11311	10485
¹⁸¹ Ta	0.16	0.29	0.29	0.19	0.27	0.25	0.11	0.16	0.10
²⁰⁷ Pb	6.79	7.33	7.21	5.08	6.95	7.76	4.82	7.52	3.50
²⁰⁸ Pb	11.8	16.8	8.96	6.27	13.6	19.4	6.32	12.7	5.42
²³² Th	229	292	154	121	245	404	101	204	110
²³⁸ U	262	312	246	201	306	388	196	299	166
<i>T_{zirc}</i> (°C)	683	654	658			704	673	804	

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Fazenda Itahy (MD-24)

	pto 31	pto 32	pto 33	pto 36	pto 40	pto 37	pto 17	pto 38	pto 8.1n
	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim-core</i>	<i>white core</i>
Th / U	0.87	0.94	0.63	0.60	0.80	1.04	0.51	0.68	0.66
U / Yb	1.8	1.7	1.2	1.0	1.4	1.4	1.1	1.0	0.9
Zr / Hf	45	45	43	43	49	47	41	44	47
La _N		1.7	0.7	0.7	0.1	11	3.4	19	0.3
Ce _N	47	56	49	42	65	87	36	103	33
Pr _N		1.7	0.9	2.7	1.5	9.8	11.7	55.8	0.9
LREE _N	47	59	51	45	66	107	51	178	34
Sm _N	8.8	12	12	19	15	16	21	95	12
(Sm / La) _N		7	16	28	117	1.5	6.2	5.0	39
Nd _N	2.3	3.1	1.6	4.5	2.7	5.9	12	69	2.6
Gd _N	40	44	59	67	50	61	39	143	48
Eu _N	15	22	30	29	17	25	34	104	21
Ce _N / Ce*		27	52	32	184	10	6.9	3.5	51
Eu _N / Eu*	0.8	1.0	1.1	0.8	0.6	0.8	1.2	0.9	0.8
Yb / Ta	943	631	744	1080	808	1150	1594	1920	1735
Y / Nb	38	47	45	53	54	55	42	66	52
Σ REE	334	416	469	462	498	638	379	774	395
Y + Σ REE	724	921	997	997	1148	1359	843	1583	932

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Fazenda Itahyé (MD-24)							
Isotope (ppm)	pto 34 <i>grey core</i>	pto 35 <i>black core</i>	pto 39 <i>black core</i>	pto 13 <i>core</i>	Median	Mean	sd
⁷ Li	4.33	<2.03	1.92	<0.48	3.28	3.64	1.55
²⁴ Mg	0.63	1.92	1.23	0.3	1.29	4.25	5.34
²⁷ Al	3.79	17.5	75.9	<2.07	13.9	30.0	29.8
²⁹ Si	191294	190356	197911	171307	173505	174248	10030
³¹ P	<65	155	386	83.4	105	138	65
⁴⁴ Ca				<209			
⁴⁵ Sc	288	364	423	282	272	283	28
⁴⁹ Ti	4.92	6.57	57.46	1.42	4.54	8.41	7.09
⁵⁵ Mn	<1.89	<3.47	6.09	<1.35	5.02	4.89	0.88
⁵⁶ Fe	<13	<24	183	<14	47.2	60.2	35.0
⁸⁵ Rb				0.16	0.19	0.25	0.10
⁸⁸ Sr	0.41	0.47	0.76	0.35	0.37	0.50	0.19
⁸⁹ Y	556	931	448	551	528	553	112
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	11.1	14.6	10.6	9.52	10.7	11.0	1.0
⁹⁵ Mo	14.6	16.3	13.6	10.5	11.5	11.8	1.6
¹³⁷ Ba	<0.20	0.61	1.59	0.14	0.61	0.95	0.64
¹³⁹ La	0.12	4.72	7.82	0.29	0.19	1.15	1.50
¹⁴⁰ Ce	30.6	73.1	102	19.7	28.6	34.8	14.9
¹⁴¹ Pr	0.22	4.98	13.0	0.19	0.22	1.40	1.91
¹⁴³ Nd	2.39	36.1	74.9	4.17	2.10	8.67	11.2
¹⁴⁷ Sm	1.52	15.1	38.8	2.13	2.13	5.09	5.05
¹⁵¹ Eu	1.26	5.13	12.8	1.74	1.33	2.26	1.63
¹⁵⁷ Gd	11.0	28.9	40.3	9.86	10.4	13.3	6.0
¹⁵⁹ Tb	3.72	7.79	6.07	3.36	3.36	3.71	1.18
¹⁶³ Dy	44.1	73.5	43.8	36.4	36.7	40.2	10.8
¹⁶⁵ Ho	17.8	26.8	12.5	15.8	15.0	15.9	3.9
¹⁶⁶ Er	88.7	119	52.7	78.7	70.5	76.9	18.1
¹⁶⁹ Tm	20.4	27.4	11.3	17.6	16.6	17.6	3.7
¹⁷³ Yb	245	292	128	192	187	199	42
¹⁷⁵ Lu	56.6	62.2	32.1	49.1	46.9	47.2	9.0
¹⁷⁹ Hf	12799	11940	12903	11224	10954	11098	721
¹⁸¹ Ta	0.31	0.59	0.04	0.10	0.17	0.20	0.08
²⁰⁷ Pb	7.35	8.28	5.32	3.04	5.32	5.57	1.39
²⁰⁸ Pb	10.2	15.4	6.68	7.52	8.96	9.70	3.31
²³² Th	216	249	198	137	164	179	60
²³⁸ U	302	327	434	195	224	248	62
<i>T_{zirc}</i>(°C)	682	705	922	594	676	692	46

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Fazenda Itahy (MD-24)

	pto 34 <i>grey core</i>	pto 35 <i>black core</i>	pto 39 <i>black core</i>	pto 13 <i>core</i>	Median	Mean	sd
Th / U	0.71	0.76	0.46	0.70	0.70	0.71	0.12
U / Yb	1.2	1.1	3.4	1.0	1.1	1.3	0.4
Zr / Hf	39	42	38	44	45	45	3
La _N	0.5	20	33	1.2	0.8	4.8	6.3
Ce _N	50	119	166	32	47	57	24
Pr _N	2.3	52.4	137	2.0	2	15	20
LREE _N	53	192	337	35	51	76	49
Sm _N	10	99	253	14	14	33	33
(Sm / La) _N	20	4.9	7.7	12	16	23	15
Nd _N	5.1	77	160	8.9	4.5	19	24
Gd _N	54	141	196	48	50	65	29
Eu _N	22	88	220	30	23	39	28
Ce _N / Ce*	46	3.8	3.0	14	28	38	27
Eu _N / Eu*	0.9	0.8	1.0	1.2	0.8	0.9	0.1
Yb / Ta	798	494	3564	1923	1080	1237	513
Y / Nb	50	64	42	58	50	50	8
Σ REE	524	777	576	431	431	467	108
Y + Σ REE	1079	1708	1024	982	982	1020	209

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Itaquí (ITQ-2)								
Isotope (ppm)	pto17n <i>core</i>	pto9-2n <i>core</i>	pto1 <i>core</i>	pto16 <i>core</i>	pto18 <i>core</i>	Median	Mean	sd
⁷ Li	1.65	6.58	20.1	5.28	2.57	12.6	15.2	9.6
²⁴ Mg	2.84	0.87	2.29	88.7	<0.82	3.91	13.6	14.3
²⁷ Al	38.4	43.1	35.9	1332	7.29	43.1	184	221
²⁹ Si	189649	171818	186226	175223	179649	181604	181301	10280
³¹ P	261	164	<95	394	97.1	125	159	78
⁴⁴ Ca	<400	<394	<450	513	<436	405	404	74
⁴⁵ Sc	262	264	276	252	251	262	265	12
⁴⁹ Ti	12.4	8.61	<2.73	129	2.24	7.98	20.8	20.5
⁵⁵ Mn	2.65	<2.38	<2.74	17.84	<2.68	3.75	6.14	4.68
⁵⁶ Fe	111	98	134	982	57.2	111	188	147
⁸⁵ Rb	0.16	<0.14	0.60	4.07	0.40	0.40	0.82	0.78
⁸⁸ Sr	3.66	0.94	2.63	8.72	0.54	1.57	2.27	1.50
⁸⁹ Y	1182	1200	554	2343	947	799	961	411
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	
⁹³ Nb	13.0	12.4	10.1	17.9	10.4	11.5	12.3	1.9
⁹⁵ Mo	13.1	10.5	10.5	10.8	12.9	10.8	10.9	1.0
¹³⁷ Ba	<0.42	0.41	0.68	2.64	<0.31	0.66	1.24	0.86
¹³⁹ La	8.86	5.51	4.14	206	1.21	8.86	26.1	32.0
¹⁴⁰ Ce	111	109	41.3	1178	55.4	95.3	184	174
¹⁴¹ Pr	8.94	5.12	3.45	190	1.73	7.68	23.2	28.6
¹⁴³ Nd	53.9	30.0	21.7	1115	11.5	45.8	137	168
¹⁴⁷ Sm	22.8	14.3	6.66	319	5.23	14.3	39.7	46.0
¹⁵¹ Eu	5.43	5.03	1.89	55.4	1.73	3.42	8.07	7.92
¹⁵⁷ Gd	43.8	35.2	12.1	207	17.1	17.1	36.8	27.9
¹⁵⁹ Tb	12.7	9.88	3.19	30.3	5.22	4.02	7.77	5.22
¹⁶³ Dy	127	112	35.5	236	65.4	50.7	78.3	47.1
¹⁶⁵ Ho	42.8	38.7	15.2	71.9	27.3	23.2	28.9	14.2
¹⁶⁶ Er	178	165	76.2	287	136	115	131	54.7
¹⁶⁹ Tm	33.2	35.6	18.4	60.0	31.8	27.7	29.4	10.5
¹⁷³ Yb	307	344	219	584	324	307	311	90
¹⁷⁵ Lu	60.0	67.8	58.5	117	75.6	60.0	69.8	18.2
¹⁷⁹ Hf	12651	11521	11764	9294	9110	11400	10996	871
¹⁸¹ Ta	1.09	0.55	0.17	1.05	0.24	0.37	0.47	0.29
²⁰⁷ Pb	13.6	24.5	18.4	24.0	6.87	22.1	20.1	5.5
²⁰⁸ Pb	22.3	64.3	17.3	46.2	16.3	22.3	28.4	12.8
²³² Th	383	553	270	1906	210	361	511	280
²³⁸ U	478	603	636	1425	236	676	772	256
<i>T_{zirc}</i> (°C)	760	728		1030	625	722	752	77

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Itaquí (ITQ-2)

	pto17n <i>core</i>	pto9-2n <i>core</i>	pto1 <i>core</i>	pto16 <i>core</i>	pto18 <i>core</i>	Median	Mean	sd
Th / U	0.80	0.92	0.43	1.34	0.89	0.5	0.6	0.3
U / Yb	1.6	1.8	2.9	2.4	0.7	2.6	2.8	0.9
Zr / Hf	39	43	42	53	54	44	46	3.8
La _N	37	23	17	869	5.1	37	110	135
Ce _N	182	178	67	1925	91	156	300	284
Pr _N	94	54	36	1999	18	81	245	301
LREE _N	313	255	121	4793	114	273	655	720
Sm _N	149	94	44	2083	34	94	260	301
(Sm / La) _N	4.0	4.0	2.5	2.4	6.7	2.5	4.0	2.2
Nd _N	115	64	46	2388	25	98	294	360
Gd _N	213	171	59	1008	83	83	179	136
Eu _N	94	87	33	955	30	59	139	136
Ce _N / Ce*	3.3	5.5	2.8	1.6	10	2.8	6.1	5.1
Eu _N / Eu*	0.5	0.7	0.6	0.7	0.6	0.7	0.7	0.1
Yb / Ta	281	626	1273	557	1345	866	844	249
Y / Nb	91	97	55	131	91	70	74	21
Σ REE	1015	977	517	4657	759	699	1111	626
Y+ Σ REE	2196	2178	1071	7000	1706	1563	2072	970

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Terra Nova (TN-1)							
Isotope (ppm)	TN-1_18a black rim	TN-1_4 grey rim	TN-1_3 grey rim	TN-1_17b grey rim	TN-1_18b grey rim	TN-1_19b grey rim	TN-1_12 black core
⁷ Li	15.8	15.1	21.5	3.80	5.92	10.3	26.4
²⁴ Mg	9.19	190	236	3.16	78.9	32.5	8.15
²⁷ Al	395	3830	3037	68.9	1958	2016	1300
²⁹ Si	173048	200893	184192	173018	182073	198807	186218
³¹ P	1665	2231	1347	406	1188	1146	2094
⁴⁴ Ca	<328	3893	1948	<221	<317	2724	777
⁴⁵ Sc	576	1877	1006	466	431	834	631
⁴⁹ Ti	53.1	886	358	7.37	97.5	236	57.8
⁵⁵ Mn	155	924	509	20.3	97.1	1098	168
⁵⁶ Fe	1802	13206	2478	221	3236	4729	4225
⁸⁵ Rb	1.73	7.56	2.8	1.08	3.45	1.58	2.51
⁸⁸ Sr	14.0	351	110	3.66	10.7	86.0	12.8
⁸⁹ Y	10534	32386	17146	3642	5831	9908	10917
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	183	3279	1229	98.0	213	392	199
⁹⁵ Mo	5.02	3.16	3.99	3.6	2.23	5.13	1.88
¹³⁷ Ba	1.6	33.6	14.5	<0.39	1.52	9.36	1.58
¹³⁹ La	18.4	95.5	42.9	1.61	29.8	96.0	28.4
¹⁴⁰ Ce	507	1802	738	140	430	1161	483
¹⁴¹ Pr	31.3	240	107	4.00	52.8	139	56.2
¹⁴³ Nd	180	1394	617	18.6	258	655	261
¹⁴⁷ Sm	144	1587	685	25.0	188	458	246
¹⁵¹ Eu	12.8	172	70.2	1.66	23.4	44.3	23.0
¹⁵⁷ Gd	355	2730	1309	69.1	387	749	462
¹⁵⁹ Tb	109	831	432	27.0	120	208	145
¹⁶³ Dy	1000	5725	3218	307	910	1543	1290
¹⁶⁵ Ho	344	1251	668	116	224	354	365
¹⁶⁶ Er	1372	3603	1901	519	772	1105	1498
¹⁶⁹ Tm	256	546	280	115	125	186	296
¹⁷³ Yb	2122	3643	1918	1072	1012	1461	2653
¹⁷⁵ Lu	403	548	292	220	192	248	505
¹⁷⁹ Hf	12451	15463	22397	15605	15311	14979	17696
¹⁸¹ Ta	9.53	68.0	69.1	6.96	5.38	6.94	11.1
²⁰⁷ Pb	66.7	37.1	16.5	18.3	23.3	19.4	59.5
²⁰⁸ Pb	243.9	86.6	20.7	26.1	46.8	36.6	104.9
²³² Th	3258	7094	3225	534	836	1364	2124
²³⁸ U	2184	3212	1869	768	677	1429	2165
<i>T_{zirc}</i> (°C)	913	1386	1197	715	990	1123	923

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Terra Nova (TN-1)

	TN-1_18a black rim	TN-1_4 grey rim	TN-1_3 grey rim	TN-1_17b grey rim	TN-1_18b grey rim	TN-1_19b grey rim	TN-1_12 black core
Th / U	1.49	2.21	1.73	0.70	1.23	0.95	0.98
U / Yb	1.0	0.9	1.0	0.7	0.7	1.0	0.8
Zr / Hf	40	32	22	32	32	33	28
La _N	77	403	181	6.8	126	405	120
Ce _N	828	2944	1206	228	703	1897	789
Pr _N	329	2523	1122	42	556	1459	591
LREE _N	1234	5870	2508	277	1385	3762	1500
Sm _N	938	10373	4479	163	1230	2991	1611
(Sm / La) _N	12	26	25	24	10	7.4	13
Nd _N	385	2986	1322	40	552	1402	558
Gd _N	1728	13284	6372	336	1881	3646	2248
Eu _N	221	2971	1210	29	403	764	397
Ce _N / Ce*	6.3	3.8	3.4	18.6	3.4	3.1	3.9
Eu _N / Eu*	0.17	0.25	0.23	0.12	0.27	0.23	0.21
Yb / Ta	223	54	28	154	188	211	240
Y / Nb	58	10	14	37	27	25	55
ΣREE	6855	24167	12278	2634	4724	8407	8311
Y+ ΣREE	17389	56553	29424	6277	10555	18315	19229

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Terra Nova (TN-1)							
Isotope (ppm)	TN-1_16 <i>black core</i>	TN-1_17n <i>black core</i>	TN-1_19n <i>black cor</i>	TN-1_2 <i>grey core</i>	Median	Mean	sd
⁷ Li	9.85	11.6	12.7	18.6	13.9	13.9	6.3
²⁴ Mg	117	82.0	66.8	7.44	72.8	85.4	82.1
²⁷ Al	7147	5700	6416	130	2527	3037	2477
²⁹ Si	200822	190546	195445	182740	185205	187260	10030
³¹ P	3416	2615	3896	1727	1749	1958	982
⁴⁴ Ca	8515	8235	9111	<252	4164	4955	3555
⁴⁵ Sc	2247	1348	1364	458	920	1057	602
⁴⁹ Ti	1075	430	581	49.8	297	361	351
⁵⁵ Mn	3099	3109	3205	88.0	716	1181	1282
⁵⁶ Fe	9095	11466	11792	264	4477	8202	9864
⁸⁵ Rb	5.85	2.91	4.69	1.51	2.67	3.18	1.94
⁸⁸ Sr	266	260	210	12.8	98.2	124	122
⁸⁹ Y	29878	20453	22342	4826	13729	15367	9495
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	1077	439	469	59.9	415	705	896
⁹⁵ Mo	2.62	3.23	2.81	2.87	3.20	3.34	1.00
¹³⁷ Ba	46.3	35.5	35.1	1.11	14.5	19.0	17.2
¹³⁹ La	158	145	364	3.24	69.2	90.1	101
¹⁴⁰ Ce	3274	3185	3404	204	950	1423	1246
¹⁴¹ Pr	508	518	425	9.69	123	195	193
¹⁴³ Nd	3355	3063	1838	57.0	636	1098	1155
¹⁴⁷ Sm	2893	1708	1068	68.3	571	860	876
¹⁵¹ Eu	246	132	96.7	7.29	57.3	78.2	76.1
¹⁵⁷ Gd	3395	1955	1609	173	1029	1237	1068
¹⁵⁹ Tb	731	415	443	61	303	327	262
¹⁶³ Dy	4584	2691	3173	550	2117	2318	1685
¹⁶⁵ Ho	964	602	750	167	483	537	341
¹⁶⁶ Er	2895	1902	2409	631	1700	1717	935
¹⁶⁹ Tm	477	332	400	118	288	288	140
¹⁷³ Yb	3654	2785	3161	988	2376	2258	981
¹⁷⁵ Lu	637	518	531	180	424	393	160
¹⁷⁹ Hf	12595	12904	13058	9541	15145	14857	3223
¹⁸¹ Ta	19.4	11.4	10.3	3.96	10.3	19.4	23.3
²⁰⁷ Pb	48.0	44.6	38.7	17.5	34.1	35.1	17.1
²⁰⁸ Pb	126.1	98.5	77.2	39.6	69.1	80.6	61.4
²³² Th	5456	3957	3371	650	3111	2905	1991
²³⁸ U	4126	3669	4213	732	2175	2322	1293
<i>T_{zirc}(°C)</i>	1432	1231	1292	905	1160	1114	223

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Terra Nova (TN-1)

	TN-1_16 <i>black core</i>	TN-1_17n <i>black core</i>	TN-1_19n <i>black core</i>	TN-1_2 <i>grey core</i>	Median	Mean	sd
Th / U	1.32	1.08	0.80	0.89	1.1	1.2	0.4
U / Yb	1.1	1.3	1.3	0.7	1.0	1.0	0.2
Zr / Hf	39	38	38	52	33	35	7
La _N	668	612	1536	14	292	380	428
Ce _N	5350	5204	5563	333	1552	2325	2036
Pr _N	5345	5449	4477	102	1291	2055	2028
LREE _N	11363	11265	11576	448	3135	4760	4412
Sm _N	18908	11165	6980	446	3735	5622	5723
(Sm / La) _N	28	18	4.5	33	19	18	8.9
Nd _N	7185	6559	3936	122	1362	2351	2472
Gd _N	16519	9514	7827	841	5009	6020	5198
Eu _N	4242	2277	1667	126	987	1349	1311
Ce _N / Ce*	3.6	3.9	2.6	11.7	3.7	5.7	4.8
Eu _N / Eu*	0.24	0.22	0.23	0.21	0.2	0.2	0.0
Yb / Ta	188	245	307	250	217	195	82
Y / Nb	28	47	48	81	32	37	21
Σ REE	27770	19951	19673	3218	10342	12819	8509
Y + Σ REE	57648	40404	42015	8044	24326	28186	17897

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Perus (Pe-04)							
Isotope (ppm)	pto1-1 <i>black core</i>	pto6-1 <i>black core</i>	pto2-1 <i>black rim</i>	pto4-1 <i>black rim</i>	spot5-1 <i>black rim</i>	pto11-1 <i>black rim</i>	pto12-1 <i>black rim</i>
⁷ Li	17.9	43.2	17.6	29.9	<199	23.4	30.1
²⁴ Mg	900	1168	872	1292	986	1533	736
²⁷ Al	4143	5739	4176	4978	7277	8002	4862
²⁹ Si	174226	170016	172196	173996	236142	199961	185632
³¹ P	9755	10730	10737	11704	<4844	11508	6892
⁴⁴ Ca	19978	21043	22146	20391	<38996	27903	15480
⁴⁵ Sc	1328	1135	1375	1194	1295	1404	944
⁴⁹ Ti	899	729	849	267	810	368	888
⁵⁵ Mn	1492	2110	1555	1574	1666	1283	2318
⁵⁶ Fe	4888	6823	5567	7752	3216	6101	3856
⁸⁵ Rb	9.0	16.6	10.4	21.6	26.2	16.7	11.0
⁸⁸ Sr	105	113	112	90	110	154	89.7
⁸⁹ Y	37890	37806	35723	30856	44048	54202	34104
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	3164	2494	2044	2024	4473	5818	4887
⁹⁵ Mo	3.01	2.57	3.79	3.51	<110	2.66	3.94
¹³⁷ Ba	1622	1355	1577	915	2548	3464	1523
¹³⁹ La	128	177	183	101	153	217	153
¹⁴⁰ Ce	2478	2643	2454	1424	3572	3270	2806
¹⁴¹ Pr	104	127	116	75	135	165	155
¹⁴³ Nd	620	693	644	487	721	1009	841
¹⁴⁷ Sm	748	781	711	617	968	1218	925
¹⁵¹ Eu	67	63.8	66	46	119	112	74.7
¹⁵⁷ Gd	1707	1870	1622	1558	2135	2788	1601
¹⁵⁹ Tb	611	662	559	528	816	949	578
¹⁶³ Dy	4984	5033	4377	4076	6941	7317	4840
¹⁶⁵ Ho	1070	1058	940	930	1378	1567	1056
¹⁶⁶ Er	3403	3328	2943	2891	4045	4678	3022
¹⁶⁹ Tm	639	586	544	521	792	809	546
¹⁷³ Yb	5323	5068	4486	4549	6590	6492	4423
¹⁷⁵ Lu	791	810	677	753	927	973	673
¹⁷⁹ Hf	25524	25784	27085	23877	23628	20952	20015
¹⁸¹ Ta	329	197	241	142	254	170	514
²⁰⁷ Pb	3498	3613	3621	3683	845	4257	2751
²⁰⁸ Pb	3280	3311	3387	3180	619	3933	2608
²³² Th	1041	2528	428	2164	1089	753	1948
²³⁸ U	8569	9160	6785	11110	13175	16284	7618
<i>T_{zirc} (°C)</i>	<i>1389</i>	<i>1341</i>	<i>1376</i>	<i>1144</i>	<i>1365</i>	<i>1202</i>	<i>1386</i>

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Perus (Pe-04)

	pto1-1 <i>black core</i>	pto6-1 <i>black core</i>	pto2-1 <i>black rim</i>	pto4-1 <i>black rim</i>	spot5-1 <i>black rim</i>	pto11-1 <i>black rim</i>	pto12-1 <i>black rim</i>
Th / U	0.12	0.28	0.06	0.19	0.08	0.05	0.26
U / Yb	1.6	1.8	1.5	2.4	2.0	2.5	1.7
Zr / Hf	19	19	18	21	21	24	25
La _N	538	746	774	427	644	914	646
Ce _N	4049	4319	4010	2328	5836	5343	4584
Pr _N	1094	1339	1218	791	1419	1742	1628
LREE _N	5681	6404	6002	3545	7900	7999	6858
Sm _N	4889	5102	4648	4033	6325	7962	6048
(Sm / La) _N	9.1	6.8	6.0	9.4	9.8	8.7	9.4
Nd _N	1328	1485	1378	1043	1543	2160	1800
Gd _N	8309	9100	7894	7583	10390	13566	7792
Eu _N	1157	1099	1141	787	2053	1937	1288
Ce _N / Ce*	5.6	4.6	4.3	4.1	6.8	4.4	5.0
Eu _N / Eu*	0.18	0.16	0.19	0.14	0.25	0.19	0.19
Yb / Ta	16	26	19	32	26	38	8.6
Y / Nb	12	15	17	15	10	9.3	7.0
Σ REE	22673	22900	20323	18555	29290	31565	21694
Y+ Σ REE	60563	60706	56046	49412	73338	85767	55798

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Isotope (ppm)	Perus (Pe-04)				Median	Mean	sd
	pto13-1 <i>black rim</i>	pto14-1 <i>black rim</i>	pto15-1 <i>black rim</i>	pto16-1 <i>black rim</i>			
⁷ Li	8.24	16.8	141	59.0	26.6	39	39
²⁴ Mg	911	917	687	1385	917	1035	272
²⁷ Al	4336	5190	6244	6186	5190	5557	1272
²⁹ Si	162062	176868	172086	188176	174226	182851	20454
³¹ P	10043	8276	7444	10342	10193	9743	3335
⁴⁴ Ca	22410	25848	29519	23672	22278	22839	7915
⁴⁵ Sc	1140	991	1112	1251	1194	1197	150
⁴⁹ Ti	861	626	484	301	729	644	247
⁵⁵ Mn	1312	3256	3398	1344	1574	1937	760
⁵⁶ Fe	5034	4494	5551	6760	5551	5458	1352
⁸⁵ Rb	8.69	6.74	28.7	19.2	16.6	15.9	7.4
⁸⁸ Sr	118	146	129	111	112	116	20
⁸⁹ Y	43093	40396	35035	33572	37806	38793	6509
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	2876	4804	4469	2813	3164	3624	1304
⁹⁵ Mo	0.98	6.36	3.27	15.8	3.39	4.59	4.18
¹³⁷ Ba	2111	1436	1550	1451	1550	1777	698
¹³⁹ La	174	183	140	143	153	159	32
¹⁴⁰ Ce	2959	4810	3047	1889	2806	2850	888
¹⁴¹ Pr	146	168	144	111	135	131	28
¹⁴³ Nd	844	956	777	596	721	744	159
¹⁴⁷ Sm	1023	1098	906	716	906	883	186
¹⁵¹ Eu	92.7	93.5	76.2	66.7	74.7	80	22
¹⁵⁷ Gd	2240	2102	1867	1649	1867	1922	371
¹⁵⁹ Tb	777	711	644	560	644	672	130
¹⁶³ Dy	5946	5895	4995	4291	4995	5336	1066
¹⁶⁵ Ho	1240	1258	1042	926	1058	1133	205
¹⁶⁶ Er	3769	3621	3192	2932	3328	3439	557
¹⁶⁹ Tm	656	665	569	551	586	625	99
¹⁷³ Yb	5219	5388	4515	4669	5068	5157	771
¹⁷⁵ Lu	788	769	691	768	769	784	95
¹⁷⁹ Hf	23988	21556	22863	21850	23628	23375	2189
¹⁸¹ Ta	230	724	428	200	241	312	177
²⁰⁷ Pb	3891	2994	2866	3552	3552	3234	910
²⁰⁸ Pb	3630	2820	2601	3108	3180	2952	873
²³² Th	839	2685	1003	1118	1089	1418	771
²³⁸ U	8883	15195	9110	9388	9160	10480	3106
<i>T_{zirc} (°C)</i>	<i>1379</i>	<i>1308</i>	<i>1255</i>	<i>1165</i>	<i>1341</i>	<i>1301</i>	<i>93</i>

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Perus (Pe-04)

Isotope (ppm)	pto13-1 <i>black rim</i>	pto14-1 <i>black rim</i>	pto15-1 <i>black rim</i>	pto16-1 <i>black rim</i>	Median	Mean	sd
Th / U	0.09	0.18	0.11	0.12	0.1	0.1	0.1
U / Yb	1.7	2.8	2.0	2.0	2.0	2.0	0.4
Zr / Hf	21	23	22	23	21	21	2
La _N	734	771	590	602	646	672	134
Ce _N	4835	7859	4980	3086	4584	4657	1451
Pr _N	1536	1763	1513	1173	1419	1383	297
LREE _N	7104	10394	7082	4861	6858	6712	1790
Sm _N	6687	7177	5919	4680	5919	5770	1213
(Sm / La) _N	9.1	9.3	10.0	7.8	9.1	8.7	1.3
Nd _N	1807	2047	1665	1275	1543	1594	340
Gd _N	10901	10230	9087	8025	9087	9352	1808
Eu _N	1598	1611	1314	1150	1288	1376	383
Ce _N / Ce*	4.9	7.4	6.0	4.0	4.9	5.2	1.1
Eu _N / Eu*	0.19	0.19	0.18	0.19	0.19	0.19	0.03
Yb / Ta	23	7.4	11	23	23	21	10
Y / Nb	15	8.4	7.8	12	12	12	3.5
Σ REE	25873	27716	22606	19867	22673	23915	4158
Y + Σ REE	68966	68112	57641	53440	60563	62708	10498

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

São Roque (SR-07)								
Isotope (ppm)	pto12 <i>rim</i>	pto15 <i>rim</i>	pto14 <i>rim</i>	pto13 <i>rim</i>	pto17-1 <i>rim</i>	pto26 <i>rim</i>	pto27 <i>rim</i>	pto22 <i>rim</i>
⁷ Li	16.0	14.9	12.0	9.1	14.0	16.5	4.4	12.0
²⁴ Mg	18.3	89.2	39.5	61.9	22.7	126	64.6	21.3
²⁷ Al	50.1	167	91.0	138	27.9	46.3	160	49.4
²⁹ Si	175740	164850	135527	147250	213998	179676	153293	168040
³¹ P	<109	308	<127	234	463	216	203	<99
⁴⁴ Ca	<535	865	<642	<819	500	<514	732	<514
⁴⁵ Sc	245	226	276	331	287	246	244	289
⁴⁹ Ti	<3.40	9.25	12.7	11.9	4.99	6.22	25.0	11.5
⁵⁵ Mn	<3.14	<4.07	<3.87	14.6	2.94	4.85	<3.76	<3.10
⁵⁶ Fe	96.5	359	70.1	353	33.1	189	275	27.3
⁸⁵ Rb	<0.15	0.71	0.29	<0.27	<0.11	<0.14	0.69	<0.17
⁸⁸ Sr	0.54	0.94	1.79	1.44	1.56	1.06	1.19	0.70
⁸⁹ Y	508	399	497	1134	497	536	1076	708
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	10.6	11.2	11.4	12.1	11.3	13.5	11.3	11.0
⁹⁵ Mo	9.03	12.9	6.90	9.44	11.2	13.2	12.4	9.12
¹³⁷ Ba	0.53	0.96	2.54	<0.58	<0.20	1.12	2.48	0.77
¹³⁹ La	1.86	1.67	4.13	3.26	2.02	3.23	1.63	1.77
¹⁴⁰ Ce	36.7	28.7	44.3	76.9	34.5	43.6	51.3	40.7
¹⁴¹ Pr	1.36	0.65	2.58	3.06	0.42	1.68	1.02	1.28
¹⁴³ Nd	13.1	4.47	25.4	25.4	2.70	10.9	11.9	6.40
¹⁴⁷ Sm	8.03	4.02	8.08	9.35	2.57	9.72	9.71	4.63
¹⁵¹ Eu	2.72	1.06	3.06	3.70	0.91	1.82	3.03	1.93
¹⁵⁷ Gd	12.9	10.6	13.8	28.4	10.2	15.3	30.4	15.9
¹⁵⁹ Tb	3.48	3.25	5.34	8.58	2.93	3.71	8.35	5.84
¹⁶³ Dy	40.6	30.5	50.2	84.8	36.3	43.7	99.0	52.0
¹⁶⁵ Ho	14.1	11.9	22.8	33.1	14.7	14.5	35.6	18.7
¹⁶⁶ Er	62.9	55.7	83.3	132	71.7	80.5	147	85.5
¹⁶⁹ Tm	16.2	14.0	16.7	28.0	16.5	19.6	29.2	20.4
¹⁷³ Yb	161	141	192	330	188	192	310	212
¹⁷⁵ Lu	36.3	31.0	44.0	76.5	46.1	41.2	64.6	49.4
¹⁷⁹ Hf	10793	10034	11594	12748	11712	10491	10307	11767
¹⁸¹ Ta	0.25	0.15	0.45	0.21	0.47	0.28	0.48	0.39
²⁰⁷ Pb	12.3	9.35	13.2	9.81	9.07	13.7	11.5	11.0
²⁰⁸ Pb	23.6	15.1	15.2	22.8	13.7	19.4	19.8	19.6
²³² Th	304	272	282	440	216	241	330	274
²³⁸ U	426	389	482	452	392	423	357	403
<i>T_{zirc}</i> (°C)		734	762	756	683	701	828	753

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

São Roque (SR-07)

	pto12 <i>rim</i>	pto15 <i>rim</i>	pto14 <i>rim</i>	pto13 <i>rim</i>	pto17-1 <i>rim</i>	pto26 <i>rim</i>	pto27 <i>rim</i>	pto22 <i>rim</i>
Th / U	0.71	0.70	0.59	0.97	0.55	0.57	0.92	0.68
U / Yb	2.64	2.76	2.51	1.37	2.09	2.20	1.15	1.90
Zr / Hf	46	49	43	39	42	47	48	42
La _N	7.8	7.0	17	14	8.5	14	6.9	7.5
Ce _N	60	47	72	126	56	71	84	66
Pr _N	14	6.8	27	32	4.4	18	11	13
LREE _N	82	61	117	172	69	102	102	87
Sm _N	52	26	53	61	17	64	63	30
(Sm / La) _N	6.7	3.7	3.0	4.4	2.0	4.7	9.2	4.1
Nd _N	28	10	54	54	5.8	23	25	14
Gd _N	63	51	67	138	50	75	148	77
Eu _N	47	18	53	64	16	31	52	33
Ce _N / Ce*	5.0	6.0	2.8	5.8	7.5	4.4	7.9	7.3
Eu _N / Eu*	0.8	0.5	0.9	0.7	0.5	0.5	0.5	0.7
Yb / Ta	650	965	427	1574	401	687	645	547
Y / Nb	48	36	43	94	44	40	95	64
ΣREE	411	338	516	843	429	481	802	516
$Y + \Sigma REE$	920	737	1013	1977	926	1017	1878	1224

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

São Roque (SR-07)							
Isotope (ppm)	pto23 <i>black core</i>	pto18-1 <i>black core</i>	pto25 <i>core</i>	pto21 <i>core</i>	Median	Mean	sd
⁷ Li	13.8	45.6	10.4	11.3	12.9	15.0	5.5
²⁴ Mg	78.8	515	6.71	<0.42	61.9	94.9	82.0
²⁷ Al	629	1247	16.8	2.95	70.6	219	240
²⁹ Si	186792	173916	160652	181204	170978	170078	15143
³¹ P	186	262	<62	87.9	225	245	74
⁴⁴ Ca	1267	2311	<329	<261	865	1135	523
⁴⁵ Sc	317	308	246	265	271	273	28
⁴⁹ Ti	134	108	3.07	2.64	11	30	33
⁵⁵ Mn	94.7	90.6	2.95	<1.53	10	35	38
⁵⁶ Fe	1165	2280	31.1	<11	189	444	465
⁸⁵ Rb	0.49	1.08	<0.121	<0.094	0.69	0.65	0.21
⁸⁸ Sr	18.3	40.0	0.39	0.62	1.13	5.70	7.80
⁸⁹ Y	1831	1274	603	460	569	793	357
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	22.2	34.0	10.1	11.0	11.3	14.1	4.7
⁹⁵ Mo	10.5	13.7	10.8	9.36	10.7	10.7	1.6
¹³⁷ Ba	30.7	29.5	0.32	<0.22	1.12	7.65	9.96
¹³⁹ La	127	155	0.55	0.47	1.94	25.2	38.6
¹⁴⁰ Ce	1052	1091	35.1	34.2	42.1	214	286
¹⁴¹ Pr	86.0	122	0.52	0.13	1.32	18.4	28.5
¹⁴³ Nd	546	887	5.43	1.47	11.4	128	196
¹⁴⁷ Sm	240	227	4.66	2.09	8.06	44.1	63.1
¹⁵¹ Eu	77.0	93.1	1.73	0.85	2.33	15.9	23.0
¹⁵⁷ Gd	206	104	14.2	9.12	14.8	39.2	38.6
¹⁵⁹ Tb	27.2	11.0	4.03	3.01	4.69	7.23	4.37
¹⁶³ Dy	197	99.2	43.5	32.3	46.9	67.4	35.0
¹⁶⁵ Ho	61.5	45.6	16.4	11.8	17.6	25.0	12.6
¹⁶⁶ Er	241	236	78.4	62.0	81.9	111	52
¹⁶⁹ Tm	49.1	48.7	16.8	14.3	18.2	24.1	9.7
¹⁷³ Yb	444	580	188	141	192	256	106
¹⁷⁵ Lu	82.6	122	43.3	31.9	45.1	55.8	20.5
¹⁷⁹ Hf	10015	12520	11105	9771	10949	11071	836
¹⁸¹ Ta	1.91	10.7	0.24	0.28	0.34	1.32	1.67
²⁰⁷ Pb	28.9	205	11.2	8.70	11.4	28.6	29.4
²⁰⁸ Pb	84.4	96.2	18.4	11.5	19.5	30.0	20.1
²³² Th	1478	507	325	232	293	409	200
²³⁸ U	954	1968	403	399	413	587	291
<i>T_{zirc} (°C)</i>	<i>1035</i>	<i>1004</i>	<i>647</i>	<i>636</i>	<i>753</i>	<i>776</i>	<i>98</i>

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

São Roque (SR-07)

	pto23 <i>black core</i>	pto18-1 <i>black core</i>	pto25 <i>core</i>	pto21 <i>core</i>	Median	Mean	sd
Th / U	1.55	0.26	0.81	0.58	0.7	0.7	0.2
U / Yb	2.15	3.40	2.14	2.84	2.2	2.3	0.5
Zr / Hf	50	40	45	51	45	45	3
La _N	536	653	2.3	2.0	8.2	106	163
Ce _N	1718	1783	57	56	69	350	467
Pr _N	905	1285	5.5	1.4	14	194	300
LREE _N	3160	3721	65	59	94	650	930
Sm _N	1568	1483	30	14	53	289	412
(Sm / La) _N	2.9	2.3	13.0	6.9	4.2	5.2	2.5
Nd _N	1169	1899	12	3	24	275	420
Gd _N	1004	505	69	44	72	191	188
Eu _N	1327	1604	30	15	40	274	397
Ce _N / Ce*	2.5	1.9	14	24	5.9	7.5	4.0
Eu _N / Eu*	1.1	1.9	0.6	0.6	0.7	0.8	0.3
Yb / Ta	232	54	774	495	596	621	262
Y / Nb	82	38	60	42	46	57	18
Σ REE	3436	3821	453	344	499	1033	865
Y+ Σ REE	5266	5096	1056	804	1036	1826	1152

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

ITU (ITU-14X)								
Isotope (ppm)	pto1-1 <i>rim</i>	pto11-1 <i>rim</i>	pto5-1 <i>rim</i>	pto12-2 <i>rim</i>	pto8-2 <i>rim</i>	spot13-2 <i>white rim</i>	pto2-1 <i>interm</i>	pto3-1 <i>interm</i>
⁷ Li	14.0	12.3	6.54	9.70	3.77	7.11	8.66	14.4
²⁴ Mg	8.28	10.2	7.37	<0.93	<0.99	20.4	76.6	10.9
²⁷ Al	154	662	102	<2.35	41	404	708	167
²⁹ Si	205501	192129	145449	167343	173929	180997	178524	199211
³¹ P	473	463	586	207	413	539	4571	1502
⁴⁴ Ca	<355	<305	431	<290	350	<232	5335	2808
⁴⁵ Sc	335	275	246	243	265	295	329	301
⁴⁹ Ti	91.46	74.9	53.8	4.37	23.8	187	485	84.0
⁵⁵ Mn	18.5	13.3	6.26	<1.18	2.64	20.0	62.4	34.0
⁵⁶ Fe	397	530	771	<24	<22	623	1421	437
⁸⁵ Rb	0.62	2.6	0.89	0.3	0.24	0.5	1.54	0.43
⁸⁸ Sr	1.32	2.86	1.19	0.36	0.55	2.18	8.05	16.1
⁸⁹ Y	1117	1195	1415	950	1073	2077	2140	1358
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	33.3	36.1	51.5	11.0	16.9	59.3	91.3	45.9
⁹⁵ Mo	3.75	2.71	2.64	<0.91	1.99	3.46	1.96	1.6
¹³⁷ Ba	3.87	4.33	0.85	<0.39	0.61	5.50	13.1	10.6
¹³⁹ La	18.9	29.9	12.0	<0.1	7.31	54.4	90.2	146
¹⁴⁰ Ce	123	244	127	31.8	78.9	588	564	724
¹⁴¹ Pr	17.9	37.8	15.1	0.26	5.34	104	101	112
¹⁴³ Nd	110	230	86.8	2.47	34.4	647	625	606
¹⁴⁷ Sm	48.1	87.4	43.9	3.68	21.6	248	254	178
¹⁵¹ Eu	5.78	12.0	6.62	0.56	3.00	43.2	30.6	23.6
¹⁵⁷ Gd	42.3	79.2	58.0	14.5	39.2	202	207	139
¹⁵⁹ Tb	12.8	16.1	13.8	5.0	10.6	38.1	34.2	25.7
¹⁶³ Dy	118	143	138	67.8	106	305	248	189
¹⁶⁵ Ho	43.1	47.0	47.0	28.1	36.2	87.1	74.1	56.2
¹⁶⁶ Er	202	207	216	139	175	338	306	233
¹⁶⁹ Tm	46.1	44.4	49.7	32.6	38.2	70.7	62.8	54.0
¹⁷³ Yb	477	421	463	303	394	656	584	509
¹⁷⁵ Lu	95.1	81.3	83.7	65.4	73.7	119	107	96.0
¹⁷⁹ Hf	14392	12147	10745	10736	10570	11367	10376	12602
¹⁸¹ Ta	5.12	8.28	4.65	3.60	3.00	4.79	5.90	5.27
²⁰⁷ Pb	47.0	14.4	11.8	8.23	7.89	13.2	13.1	16.7
²⁰⁸ Pb	51.7	25.5	31.8	16.8	16.3	28.9	27.7	34.8
²³² Th	510	581	863	326	330	1649	1134	969
²³⁸ U	518	590	508	344	302	962	641	713
<i>T_{zirc} (°C)</i>	982	955	914	673	823	1086	1255	970

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

ITU (ITU-14X)

	pto1-1	pto11-1	pto5-1	pto12- 2	pto8-2	spot13-2	pto2-1	pto3-1
	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>white rim</i>	<i>interm</i>	<i>interm</i>
Th / U	0.99	0.98	1.70	0.95	1.09	1.71	1.77	1.36
U / Yb	1.1	1.4	1.1	1.1	0.8	1.5	1.1	1.4
Zr / Hf	34	41	46	46	47	44	48	39
La _N	80	126	50		31	230	381	615
Ce _N	200	399	207	52	129	961	921	1182
Pr _N	188	398	159	2.7	56	1099	1068	1183
LREE _N	468	923	417	55	216	2290	2370	2981
Sm _N	314	571	287	24	141	1621	1661	1165
(Sm / La) _N	3.9	4.5	5.7		4.6	7.1	4.4	1.9
Nd _N	236	493	186	5.3	74	1386	1338	1298
Gd _N	206	385	282	71	191	984	1005	675
Eu _N	100	207	114	10	52	745	528	406
Ce _N / Ce*	1.7	2.0	2.7		3.1	2.3	1.6	1.5
Eu _N / Eu*	0.4	0.4	0.4	0.2	0.3	0.6	0.4	0.5
Yb / Ta	93	51	99	84	131	137	99	97
Y / Nb	34	33	27	87	64	35	23	30
ΣREE	1360	1679	1360	694	1023	3501	3287	3091
Y+ ΣREE	2477	2874	2775	1644	2097	5578	5427	4450

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

ITU (ITU-14X)							
Isotope (ppm)	pto4-1 Interm.	pto7-2 Interm.	pto10-1 white core	pto5-2 white core	pto6-1 white core	pto8-1 white core	pto9-1 white core
⁷ Li	8.17	3.98	<1.36	3.76	1.50	2.24	4.40
²⁴ Mg	76.0	17.1	<0.70	78.7	<0.64	6.17	35.3
²⁷ Al	436	3566	85	1370	3	25	197
²⁹ Si	184380	200863	164957	219212	192347	175491	172750
³¹ P	2410	1142	434	938	233	276	427
⁴⁴ Ca	2522	644	<247	478	<260	<227	<255
⁴⁵ Sc	315	327	288	380	308	281	269
⁴⁹ Ti	144	54.8	20.5	264	17.5	17.6	106
⁵⁵ Mn	45.4	24.3	<0.99	27.7	<1.06	2.31	25.4
⁵⁶ Fe	1366	809	<21	1732	63	83	643
⁸⁵ Rb	0.6	28.42	0.47	12.8	0.45	<0.174	0.42
⁸⁸ Sr	4.26	3.31	0.98	2.99	0.31	0.25	1.18
⁸⁹ Y	1935	1369	1224	3834	1110	800	1674
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	75.7	21.0	4.61	70.0	3.71	8.98	40.5
⁹⁵ Mo	2.36	2.32	2.21	3.39	2.97	2.67	1.85
¹³⁷ Ba	6.45	22.9	1.39	9.47	<0.40	<0.36	1.97
¹³⁹ La	61.6	19.8	2.18	29.8	0.06	3.3	15.7
¹⁴⁰ Ce	375	151	34.2	453	34.6	50.0	282
¹⁴¹ Pr	57.5	20.3	1.12	73.2	0.23	3.86	45.2
¹⁴³ Nd	343	133	11.3	451	4.20	24.4	297
¹⁴⁷ Sm	167	59.1	9.55	233	8.53	20.5	154
¹⁵¹ Eu	28.1	8.20	2.29	47.9	1.91	2.96	17.3
¹⁵⁷ Gd	159	69.6	38.3	267	31.0	26.3	156
¹⁵⁹ Tb	31.1	16.2	12.8	65.6	10.0	7.8	31.3
¹⁶³ Dy	257	141	142	563	115	77.2	239
¹⁶⁵ Ho	75.4	48.6	48.5	164	42.0	27.7	66.0
¹⁶⁶ Er	331	212	210	602	171	127	254
¹⁶⁹ Tm	70.6	41.8	42.0	108	34.8	26.5	48.7
¹⁷³ Yb	689	396	378	964	311	267	460
¹⁷⁵ Lu	127	76.7	68.8	176	66.1	49.8	85.5
¹⁷⁹ Hf	13097	10197	8479	9090	10199	8839	9563
¹⁸¹ Ta	7.96	2.31	0.97	3.66	1.24	1.62	4.27
²⁰⁷ Pb	18.2	7.76	2.00	14.1	3.29	4.55	4.87
²⁰⁸ Pb	38.2	18.0	7.48	42.2	8.98	10.7	15.7
²³² Th	1118	571	146	1867	150	185	752
²³⁸ U	683	330	90	639	138	140	481
<i>T_{zirc}</i> (°C)	1046	916	808	1143	793	793	1001

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

ITU (ITU-14X)

	pto4-1	pto7-2	pto10-1	pto5-2	pto6-1	pto8-1	pto9-1
	Interm.	Interm.	white core	white core	white core	white core	white core
Th / U	1.64	1.73	1.62	2.92	1.09	1.32	1.56
U / Yb	1.0	0.8	0.2	0.7	0.4	0.5	1.0
Zr / Hf	38	49	59	55	49	56	52
La _N	260	84	9.2	126	0.3	14	66
Ce _N	613	247	56	740	57	82	460
Pr _N	605	214	12	771	2.4	41	475
LREE _N	1478	545	77	1636	59	136	1002
Sm _N	1092	386	62	1523	56	134	1007
(Sm / La) _N	4.2	4.6	6.8	12	213	10	15
Nd _N	734	285	24	966	9.0	52	636
Gd _N	776	339	186	1301	151	128	760
Eu _N	485	141	39	826	33	51	298
Ce _N / Ce*	1.7	2.0	4.4	3.0	66.5	3.8	3.3
Eu _N / Eu*	0.5	0.4	0.4	0.6	0.4	0.4	0.3
Yb / Ta	87	171	389	263	251	165	108
Y / Nb	26	65	265	55	299	89	41
Σ REE	2772	1393	1000	4197	830	714	2152
Y+ Σ REE	4707	2762	2224	8031	1940	1514	3826

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Isotope (ppm)	ITU (ITU-14X)			Median	Mean	sd
	pto6-2 <i>white core</i>	pto12-1 <i>black core</i>	pto11-2 <i>black core</i>			
⁷ Li	<1.33	10.46	11.9	7.64	7.68	4.64
²⁴ Mg	0.7	15.4	78	16.2	31.5	30.4
²⁷ Al	<1.86	403	487	300	551	843
²⁹ Si	150614	175714	161532	177119	180052	19139
³¹ P	203	772	811	506	911	1065
⁴⁴ Ca	<217	<327	313	561	1610	1425
⁴⁵ Sc	247	292	277	290	293	36
⁴⁹ Ti	12.9	306	310	79.4	125.3	134.3
⁵⁵ Mn	<0.83	47.3	50.2	24.8	27.1	20.0
⁵⁶ Fe	<15.80	657	1439	650	784	563
⁸⁵ Rb	0.215	0.95	1.89	0.60	3.14	6.99
⁸⁸ Sr	0.207	2.32	5.46	1.75	2.99	3.87
⁸⁹ Y	878	2221	3072	1364	1636	802
⁹¹ Zr	496007	496007	496007	496007	496007	
⁹³ Nb	3.11	54.0	109	38.3	40.9	31.7
⁹⁵ Mo	1.71	1.68	3.04	2.36	2.49	0.87
¹³⁷ Ba	<0.30	4.87	28.4	5.19	8.16	8.10
¹³⁹ La	0.057	26.0	41.6	19.8	32.9	37.8
¹⁴⁰ Ce	24.5	351	517	198	264	227
¹⁴¹ Pr	0.33	64.2	85.8	29.1	41.5	40.2
¹⁴³ Nd	4.64	411	509	182	252	238
¹⁴⁷ Sm	6.04	213	236	73.2	110.7	97.3
¹⁵¹ Eu	1.71	25.2	31.0	10.1	16.2	15.2
¹⁵⁷ Gd	22.5	196	235	74.4	110.1	84.4
¹⁵⁹ Tb	7.88	37.3	48.3	16.2	23.6	16.5
¹⁶³ Dy	82.0	290	377	142	200	127
¹⁶⁵ Ho	30.2	88.8	111	48.6	62.3	34.4
¹⁶⁶ Er	126	352	462	214	259	123
¹⁶⁹ Tm	26.5	69.7	95.8	47.4	53.5	22.5
¹⁷³ Yb	239	632	892	461	502	203
¹⁷⁵ Lu	48.5	128	152	84.6	94.3	34.5
¹⁷⁹ Hf	8699	12318	9767	10473	10732	1643
¹⁸¹ Ta	0.51	4.57	14.5	4.42	4.57	3.30
²⁰⁷ Pb	1.64	16.1	21.6	12.4	12.6	10.4
²⁰⁸ Pb	5.44	34.8	89.4	26.6	28.0	20.1
²³² Th	91	860	1672	666	765	554
²³⁸ U	70	640	1043	513	491	283
<i>T_{zirc} (°C)</i>	<i>764</i>	<i>1168</i>	<i>1171</i>	<i>963</i>	<i>959</i>	<i>164</i>

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

ITU (ITU-14X)

	pto6-2 <i>white core</i>	pto12-1 <i>black core</i>	pto11-2 <i>black core</i>	Median	Mean	sd
Th / U	1.30	1.34	1.60	1.5	1.5	0.5
U / Yb	0.3	1.0	1.2	1.0	0.9	0.4
Zr / Hf	57	40	51	47	47	6.9
La _N	0.2	110	175	84	139	161
Ce _N	40	573	844	323	431	371
Pr _N	3.5	676	903	306	437	423
LREE _N	44	1359	1923	734	999	934
Sm _N	39	1391	1545	479	723	636
(Sm / La) _N	164	13	8.8	6.8	28	61
Nd _N	10	879	1090	389	539	510
Gd _N	110	952	1144	362	536	411
Eu _N	29	435	535	174	280	262
Ce _N / Ce*	48	2.6	2.6	2.6	9.0	19
Eu _N / Eu*	0.4	0.4	0.4	0.4	0.4	0.1
Yb / Ta	468	138	61	120	161	114
Y / Nb	282	41	28	41	85	93
Σ REE	620	2884	3793	1536	2019	1198
Y+ Σ REE	1498	5104	6865	2824	3655	1947

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Tico-Tico (Tico-2)								
Isotope (ppm)	Tico-2_1 <i>rim-core</i>	Tico-2_2 <i>rim</i>	Tico-2_3 <i>rim-core</i>	Tico-2_4 <i>rim-core</i>	Tico-2_5 <i>rim-core</i>	Tico-2_6 <i>rim-core</i>	Tico-2_7 <i>rim</i>	Tico-2_14 <i>rim</i>
⁷ Li	7.93	5.14	2.88	6.78	5.02	<2.07	9.91	6.03
²⁴ Mg	2.66	<1.37	<1.24	<1.35	<0.75	<1.20	<1.81	<1.14
²⁷ Al	107	12.1	3.08	5.05	23.3	7.58	4.07	24.1
²⁹ Si	161318	179971	167964	181180	131812	154101	171339	166039
³¹ P	640	648	323	785	360	155	381	375
⁴⁴ Ca	424	<287.62	<252.04	<261.18	<191.29	<238.49	<297.40	<225.87
⁴⁵ Sc	334	368	294	382	288	247	275	300
⁴⁹ Ti	8.92	8.98	5.2	4.12	10.9	8.97	<3.77	<3.40
⁵⁵ Mn	8.94	<1.25	<1.14	<1.16	<0.88	1.26	1.34	<1.05
⁵⁶ Fe	199	<24	<22	<23	36.5	<21	104	<20
⁸⁵ Rb	0.58	<0.25	<0.24	0.49	<0.18	<0.216	<0.29	0.29
⁸⁸ Sr	2.12	0.46	0.25	0.51	0.24	0.23	0.23	<0.11
⁸⁹ Y	2062	1794	1198	2085	1140	811	925	680
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	6.30	5.94	5.41	4.42	3.45	3.83	7.39	3.55
⁹⁵ Mo	2.91	3.43	1.54	3.15	4.34	2.71	2.73	2.57
¹³⁷ Ba	0.77	<0.52	<0.43	0.28	<0.34	<0.36	<0.54	0.46
¹³⁹ La	3.43	0.246	<0.06	0.062	<0.05	0.315	0.422	0.37
¹⁴⁰ Ce	28.5	15.3	12.9	7.4	10.2	14.7	18.0	5.4
¹⁴¹ Pr	3.98	0.54	0.18	0.11	0.31	0.60	0.35	0.35
¹⁴³ Nd	25.0	7.75	3.76	2.59	3.89	5.56	3.15	2.69
¹⁴⁷ Sm	18.3	13.9	7.13	8.21	5.64	6.47	4.09	2.10
¹⁵¹ Eu	1.35	0.71	0.90	0.33	0.33	1.26	0.57	0.31
¹⁵⁷ Gd	56.8	52.9	31.1	50.7	24.6	24.5	18.5	12.7
¹⁵⁹ Tb	17.8	17.6	10.5	19.6	9.21	7.40	7.47	5.31
¹⁶³ Dy	178	184	115	224	104	74.5	86.8	65.0
¹⁶⁵ Ho	60.6	58.8	40.2	75.6	36.7	25.3	32.0	21.4
¹⁶⁶ Er	249	237	160	295	158	106	144	89.8
¹⁶⁹ Tm	50.4	44.3	32.2	53.4	29.9	20.4	29.8	16.0
¹⁷³ Yb	468	368	270	431	263	190	261	152
¹⁷⁵ Lu	91.1	71.5	55.5	77.9	50.0	37.1	49.9	26.9
¹⁷⁹ Hf	11639	10742	11107	12830	11060	8994	10945	10923
¹⁸¹ Ta	2.12	1.11	1.37	1.23	0.72	0.66	2.66	0.95
²⁰⁷ Pb	13.15	5.88	8.24	9.82	2.65	4.35	10.63	3.90
²⁰⁸ Pb	6.53	11.83	8.18	8.50	3.60	8.25	9.95	2.52
²³² Th	123	205	141	139	72	105	148	27.6
²³⁸ U	515	290	314	419	141	143	377	192
<i>T_{zirc}</i> (°C)	731	732	687	669	748	732		

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Tico-Tico (Tico-2)

	Tico-2_1	Tico-2_2	Tico-2_3	Tico-2_4	Tico-2_5	Tico-2_6	Tico-2_7	Tico-2_14
	<i>rim-core</i>	<i>rim</i>	<i>rim-core</i>	<i>rim-core</i>	<i>rim-core</i>	<i>rim-core</i>	<i>rim</i>	<i>rim</i>
Th / U	0.24	0.71	0.45	0.33	0.51	0.74	0.39	0.14
U / Yb	1.1	0.8	1.2	1.0	0.5	0.8	1.4	1.3
Zr / Hf	43	46	45	39	45	55	45	45
La _N	14	1.0		0.3		1.3	1.8	1.6
Ce _N	47	25	21	12	17	24	29	8.8
Pr _N	42	5.7	1.9	1.1	3.2	6.3	3.7	3.7
LREE _N	103	32	23	14	20	32	35	14
Sm _N	120	91	47	54	37	42	27	14
(Sm / La) _N	8.3	88		205		32	15	8.8
Nd _N	54	17	8.1	5.5	8.3	12	6.7	5.8
Gd _N	276	258	151	246	120	119	90	62
Eu _N	23	12	16	5.7	5.7	22	10	5.3
Ce _N / Ce*	2.1	10		17		8.7	11	3.7
Eu _N / Eu*	0.13	0.08	0.18	0.05	0.09	0.31	0.20	0.18
Yb / Ta	221	332	197	350	366	287	98	160
Y / Nb	327	302	221	472	330	212	125	192
Σ REE	1253	1073	740	1245	696	514	656	400
Y + Σ REE	3315	2867	1938	3330	1836	1325	1581	1081

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Tico-Tico (Tico-2)							
Isotope (ppm)	Tico-2_8 <i>rim</i>	Tico-2_15 <i>black rim</i>	Tico-2_16 <i>black rim</i>	Tico-2_17 <i>black rim</i>	Tico-2_21 <i>black rim</i>	Tico-2_23 <i>black rim</i>	Tico-2_18 <i>white rim</i>
⁷ Li	9.70	14.8	26.0	9.49	6.77	21.2	3.38
²⁴ Mg	1.51	69.3	37.1	69.14	148	86.8	<1.33
²⁷ Al	43.7	6412	2400	5833	9676	4289	12.4
²⁹ Si	145394	181978	178699	147148	175378	179906	158861
³¹ P	464	4554	2256	2789	4034	2874	224
⁴⁴ Ca	<174	12470	4604	14956	23697	14153	<231
⁴⁵ Sc	319	1113	610	939	1354	745	291
⁴⁹ Ti	6.69	915	226	842	733	369	7.18
⁵⁵ Mn	<0.81	1358	638	1483	1901	890	<1.09
⁵⁶ Fe	39.8	7388	4628	7017	10655	6330	<21
⁸⁵ Rb	0.37	8.40	3.50	4.02	6.09	3.38	0.44
⁸⁸ Sr	0.35	69.5	26.1	73.6	109	48.4	0.15
⁸⁹ Y	1221	29529	7315	18730	21352	10984	859
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	6.04	337	65.7	156	178	97.4	3.89
⁹⁵ Mo	2.63	3.46	6.60	5.34	7.99	5.83	3.49
¹³⁷ Ba	0.81	47.5	16.8	46.8	77.0	42.1	<0.43
¹³⁹ La	0.87	271	95.0	278	417	156	<0.04
¹⁴⁰ Ce	14.2	2601	767	2261	3282	1184	11.9
¹⁴¹ Pr	1.49	370	115	342	469	178	0.20
¹⁴³ Nd	7.25	1744	491	1516	2057	783	2.50
¹⁴⁷ Sm	7.45	824	183	636	801	302	7.00
¹⁵¹ Eu	0.44	32.3	9.6	26.7	34.6	16.7	1.32
¹⁵⁷ Gd	24.4	1416	283	988	1194	493	29.0
¹⁵⁹ Tb	8.88	501	90.7	327	370	159	9.65
¹⁶³ Dy	110	4154	772	2691	3029	1295	93.2
¹⁶⁵ Ho	38.2	937	210	562	679	314	29.1
¹⁶⁶ Er	162	2714	796	1653	2081	995	104
¹⁶⁹ Tm	30.2	441	156	277	344	157	17.6
¹⁷³ Yb	235	3226	1298	2076	2698	1329	145
¹⁷⁵ Lu	46.3	445	221	294	418	213	27.4
¹⁷⁹ Hf	8477	17346	15203	21005	21295	14998	9913
¹⁸¹ Ta	1.02	24	6.91	11.3	16.6	9.6	0.43
²⁰⁷ Pb	5.08	338	57.3	169	89.2	51.5	3.90
²⁰⁸ Pb	4.22	318	37.8	151	61.3	36.8	4.79
²³² Th	79.8	404	319	488	359	684	69.0
²³⁸ U	236	4938	2317	4254	5131	4045	146
<i>T_{zirc}</i> (°C)	707	1393	1117	1374	1342	1203	713

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Tico-Tico (Tico-2)

	Tico-2_8	Tico-2_15	Tico-2_16	Tico-2_17	Tico-2_21	Tico-2_23	Tico-2_18
	<i>rim</i>	<i>black rim</i>	<i>black rim</i>	<i>black rim</i>	<i>black rim</i>	<i>black rim</i>	<i>white rim</i>
Th / U	0.34	0.08	0.14	0.11	0.07	0.17	0.47
U / Yb	1.0	1.5	1.8	2.0	1.9	3.0	1.0
Zr / Hf	59	29	33	24	23	33	50
La _N	3.7	1144	401	1173	1758	656	
Ce _N	23	4249	1252	3695	5362	1935	20
Pr _N	16	3892	1208	3601	4936	1872	2.1
LREE _N	43	9285	2861	8469	12056	4463	22
Sm _N	49	5388	1198	4154	5238	1977	46
(Sm / La) _N	13	4.7	3.0	3.5	3.0	3.0	
Nd _N	16	3735	1052	3247	4405	1676	5.4
Gd _N	119	6891	1378	4808	5810	2397	141
Eu _N	7.6	557	165	461	597	287	23
Ce _N / Ce*	3.9	2.5	2.3	2.2	2.2	2.2	
Eu _N / Eu*	0.10	0.09	0.13	0.10	0.11	0.13	0.28
Yb / Ta	230	135	188	184	163	139	338
Y / Nb	202	88	111	120	120	113	221
Σ REE	686	19675	5487	13927	17871	7573	478
Y+ Σ REE	1907	49204	12802	32657	39223	18557	1337

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Isotope (ppm)	Tico-Tico (Tico-2)			Median	Mean	sd
	Tico-2_19 <i>white rim</i>	Tico-2_20 <i>white rim</i>	Tico-2_22 <i>white rim</i>			
⁷ Li	<2.08	8.82	4.73	7.36	9.28	6.7
²⁴ Mg	1.67	1.49	<0.87	37.1	46.4	42.5
²⁷ Al	63.9	61.3	10.2	33.9	1611	2933
²⁹ Si	166062	156892	169625	167013	165204	14150
³¹ P	183	378	276	423	1206	1424
⁴⁴ Ca	<245	<199	<221	13312	11717	7227
⁴⁵ Sc	286	292	298	309	485	332
⁴⁹ Ti	19.2	10.6	11.9	10.8	199	317
⁵⁵ Mn	1.85	1.45	1.06	8.94	571	626
⁵⁶ Fe	134	<18	53	199	3326	3469
⁸⁵ Rb	0.41	0.48	0.17	0.49	2.20	2.5
⁸⁸ Sr	0.68	0.35	0.19	0.46	19.6	33.5
⁸⁹ Y	649	773	578	1210	5705	8701
⁹¹ Zr	496007	496007	496007	496007	496007	
⁹³ Nb	4.53	4.39	5.3	5.68	49.9	90.4
⁹⁵ Mo	<0.79	3.78	2.08	3.43	3.80	1.9
¹³⁷ Ba	<0.32	0.41	<0.55	8.79	23.3	23.5
¹³⁹ La	1.53	0.71	0.25	0.87	81.6	127
¹⁴⁰ Ce	23.0	12.3	19.1	16.7	572	1050
¹⁴¹ Pr	1.81	0.38	0.27	0.57	82.4	153
¹⁴³ Nd	14.9	3.11	2.66	6.41	371	684
¹⁴⁷ Sm	8.61	4.50	5.07	7.83	158	287
¹⁵¹ Eu	0.69	0.63	0.36	0.81	7.17	11.9
¹⁵⁷ Gd	28.2	20.2	19.7	30.0	265	453
¹⁵⁹ Tb	7.85	6.6	5.88	10.1	87.8	152
¹⁶³ Dy	72.7	75.2	60	113	743	1241
¹⁶⁵ Ho	19.8	26.8	18.9	39.2	177	272
¹⁶⁶ Er	89.9	117	74.2	161	568	790
¹⁶⁹ Tm	17.1	22.6	14.4	31.2	97.4	128
¹⁷³ Yb	127	207	115	267	770	962
¹⁷⁵ Lu	29.1	39.5	22.8	52.7	123	136
¹⁷⁹ Hf	9999	9838	9457	11002	12543	3890
¹⁸¹ Ta	0.49	0.80	0.80	1.17	4.59	6.7
²⁰⁷ Pb	5.56	3.39	3.22	7.06	43.6	85.1
²⁰⁸ Pb	8.07	4.91	7.17	8.22	38.5	78.3
²³² Th	70.3	78.9	129	134	202	178
²³⁸ U	70.5	149	123	302	1322	1879
<i>T_{zirc} (°C)</i>	802	746	757	747	903	275

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Tico-Tico (Tico-2)

	Tico-2_19 <i>white rim</i>	Tico-2_20 <i>white rim</i>	Tico-2_22 <i>white rim</i>	Median	Mean	sd
Th / U	1.00	0.53	1.05	0.4	0.4	0.3
U / Yb	0.6	0.7	1.1	1.1	1.3	0.6
Zr / Hf	50	50	52	45	43	10
La _N	6.5	3.0	1.1	3.7	344	572
Ce _N	38	20	31	27	934	1716
Pr _N	19	4.0	2.8	6.0	868	1607
LREE _N	63	27	35	35	2089	3857
Sm _N	56	29	33	51	1033	1877
(Sm / La) _N	8.7	10	31	8.8	29	53
Nd _N	32	6.7	5.7	14	794	1464
Gd _N	137	98	96	146	1289	2202
Eu _N	12	11	6	14	124	205
Ce _N / Ce*	3.4	5.1	17	3.7	6.1	5.2
Eu _N / Eu*	0.14	0.20	0.11	0.1	0.1	0.1
Yb / Ta	259	259	144	209	225	83
Y / Nb	143	176	109	184	199	102
Σ REE	442	537	358	718	4090	6391
Y+ Σ REE	1091	1310	937	1923	9794	15068

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Itaquera (ITA-2)								
Isotope (ppm)	pto1-1 <i>rim</i>	pto2-1 <i>rim</i>	pto3-1 <i>rim</i>	pto5-1b <i>rim</i>	pto6-1 <i>rim</i>	pto7-1 <i>rim</i>	pto8-1 <i>rim</i>	pto13-1 <i>rim</i>
⁷ Li	11.7	21.3	15.9	12.8	10.3	17.6	11.9	22.5
²⁴ Mg	5.82	7.12	84.2	2.81	1.8	1.23	6.85	14.6
²⁷ Al	57.1	174	1181	39.0	19.8	16.3	121	319
²⁹ Si	183764	197972	197188	184098	180563	179300	196870	189680
³¹ P	609	1661	5546	1320	997	835	2029	2174
⁴⁴ Ca	<396	895	13313	712	<313	<483	1092	3380
⁴⁵ Sc	340	464	376	386	433	348	372	419
⁴⁹ Ti	13.8	12.7	137	6.55	3.22	8.74	14.0	31.6
⁵⁵ Mn	6.47	48.6	65.7	4.84	<1.75	<2.72	20.77	19.1
⁵⁶ Fe	103	177	1245	216	53.0	81.4	179	201
⁸⁵ Rb	0.64	1.03	1.89	1.15	0.71	0.50	0.42	1.26
⁸⁸ Sr	1.65	7.95	11.6	1.23	1.48	1.42	3.45	6.17
⁸⁹ Y	2223	4187	2499	2912	3910	3303	2947	4139
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	27.9	78.4	24.0	19.6	36.3	42.8	43.7	130
⁹⁵ Mo	9.95	10.3	11.9	10.8	10.7	7.04	9.15	13.0
¹³⁷ Ba	0.93	2.37	0.56	<0.37	<0.25	<0.43	1.39	3.97
¹³⁹ La	5.83	14.1	94.9	4.16	2.65	1.68	24.8	31.0
¹⁴⁰ Ce	45.8	119	211	30.2	50.4	39.4	113	166
¹⁴¹ Pr	3.68	12.1	20.2	1.84	1.36	1.48	13.3	20.3
¹⁴³ Nd	19.1	77.5	102	10.7	9.58	8.91	63.1	105
¹⁴⁷ Sm	14.8	45.9	31.7	11.5	12.9	11.9	36.1	66.8
¹⁵¹ Eu	1.79	4.7	4.43	0.66	0.95	0.84	4.45	8.23
¹⁵⁷ Gd	56.2	105	69.8	54.2	82.0	57.3	92.2	147
¹⁵⁹ Tb	19.1	36.4	23.3	20.7	30.8	21.5	30.4	49.8
¹⁶³ Dy	214	380	235	241	346	257	285	453
¹⁶⁵ Ho	78.2	141	84.4	92.4	126	93.3	97.3	140
¹⁶⁶ Er	345	604	359	405	536	410	407	540
¹⁶⁹ Tm	66.7	120	68.9	83.1	103	81.7	75.8	104
¹⁷³ Yb	612	1087	624	763	931	770	714	949
¹⁷⁵ Lu	118	210	122	151	177	151	134	168
¹⁷⁹ Hf	13615	13592	13159	12596	11911	12843	12825	12735
¹⁸¹ Ta	4.51	6.56	3.54	2.94	7.61	7.53	6.56	11.1
²⁰⁷ Pb	34.7	58.4	31.2	32.5	62.2	71.6	53.0	89.4
²⁰⁸ Pb	44.8	70.5	54.7	38.9	111	104	67.1	105
²³² Th	745	1270	885	741	2093	1891	1126	1587
²³⁸ U	1264	2869	1092	1417	2721	2821	1624	3011
<i>T_{zirc}</i> (°C)	770	762	1039	705	650	729	771	853

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Itaquera (ITA-2)

	pto1-1	pto2-1	pto3-1	pto5-1b	pto6-1	pto7-1	pto8-1	pto13-1
	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>
Th / U	0.59	0.44	0.81	0.52	0.77	0.67	0.69	0.53
U / Yb	2.1	2.6	1.7	1.9	2.9	3.7	2.3	3.2
Zr / Hf	36	36	38	39	42	39	39	39
La _N	21	107	322	15	21	164	152	72
Ce _N	63	352	276	42	75	365	245	162
Pr _N	33	269	171	16	23	329	206	101
LREE _N	116	729	769	73	119	858	603	334
Sm _N	81	565	166	63	93	612	265	197
(Sm / La) _N	3.9	5.3	0.5	4.2	4.5	3.7	1.7	2.8
Nd _N	34	350	174	19	27	356	207	95
Gd _N	232	769	268	224	357	787	419	411
Eu _N	26	215	62	9	15	267	145	60
Ce _N / Ce*	2.6	2.2	1.1	2.6	3.3	1.7	1.4	2.1
Eu _N / Eu*	0.19	0.33	0.29	0.08	0.08	0.38	0.43	0.21
Yb / Ta	136	166	176	260	122	102	109	86
Y / Nb	80	53	104	149	108	77	67	32
Σ REE	1600	2957	2050	1870	2409	1905	2089	2949
Y + Σ REE	3822	7144	4549	4781	6320	5208	5037	7088

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Itaquera (ITA-2)							
Isotope (ppm)	pto15-1 <i>rim</i>	pto4-1 <i>core</i>	pto11-1 <i>core</i>	pto16-1 <i>core</i>	Median	Mean	sd
⁷ Li	46.6	12.1	6.54	4.67	12.4	16.2	7.2
²⁴ Mg	110.6	16.1	11.5	7.58	7.4	22.5	24.9
²⁷ Al	1525	344	132	124	128	338	339
²⁹ Si	175054	180381	191644	197065	186889	187798	7272
³¹ P	995	1146	496	472	1071	1523	886
⁴⁴ Ca	4876	1266	<429	563	1179	3262	2946
⁴⁵ Sc	354	411	292	274	374	372	43
⁴⁹ Ti	155	5.71	12.6	13.4	13.0	34.5	37.2
⁵⁵ Mn	238	9.65	3.43	6.8	14.4	42.3	45.1
⁵⁶ Fe	1291	138	105	58	158	321	316
⁸⁵ Rb	2.61	1.52	0.25	0.82	0.93	1.07	0.52
⁸⁸ Sr	32.18	2.15	2.38	2.24	2.31	6.16	5.55
⁸⁹ Y	4614	3424	1479	2757	3125	3200	730
⁹¹ Zr	496007	496007	496007	496007	496007	496007	0.0
⁹³ Nb	314	19.0	26.3	21.5	32.1	65.3	54.4
⁹⁵ Mo	10.9	10.6	10.3	9.32	10.5	10.3	1.0
¹³⁷ Ba	6.84	0.59	0.45	2.06	1.39	2.13	1.51
¹³⁹ La	119	7.13	13.9	9.92	11.9	27.4	27.1
¹⁴⁰ Ce	768	47.2	55.3	75.8	65.5	143	119
¹⁴¹ Pr	83.4	2.27	4.95	9.56	7.26	14.5	13.4
¹⁴³ Nd	392	14.7	25.1	55.8	40.4	73.6	63.6
¹⁴⁷ Sm	177	18.7	10.97	30.7	24.7	39.1	28.8
¹⁵¹ Eu	28.9	0.8	1.46	4.21	3.00	5.12	4.49
¹⁵⁷ Gd	246	82.2	35.4	76.4	79.2	92.0	37.1
¹⁵⁹ Tb	72.7	29.3	13.3	23.2	26.3	30.9	11.0
¹⁶³ Dy	627	315	139	242	271	311	94
¹⁶⁵ Ho	180	111	51.7	85.3	95.3	107	27
¹⁶⁶ Er	627	472	200	380	408	440	96
¹⁶⁹ Tm	117	91.5	40.1	72.3	82.4	85.3	18.1
¹⁷³ Yb	1049	844	368	686	766	783	158
¹⁷⁵ Lu	179	165	73	139	151	149	26
¹⁷⁹ Hf	14474	11711	12749	10704	12787	12743	676
¹⁸¹ Ta	14.5	3.34	2.74	2.84	5.5	6.14	2.83
²⁰⁷ Pb	129	31.7	17.0	87.3	55.7	58.1	24.8
²⁰⁸ Pb	132	58.3	12.1	50.6	62.7	70.7	28.2
²³² Th	1320	1086	198	409	1106	1113	435
²³⁸ U	3166	1488	736	656	1556	1905	843
<i>T_{zirc} (°C)</i>	<i>1057</i>	<i>694</i>	<i>761</i>	<i>768</i>	<i>765</i>	<i>797</i>	<i>93</i>

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Itaquera (ITA-2)

	pto15-1 <i>rim</i>	pto4-1 <i>core</i>	pto11-1 <i>core</i>	pto16-1 <i>core</i>	Median	Mean	sd
Th / U	0.42	0.73	0.27	0.62	0.71	0.58	0.13
U / Yb	3.0	1.8	2.0	1.0	2.0	2.4	0.6
Zr / Hf	34	42	39	46	39	39	2
La _N	627	23	99	52	85	139	118
Ce _N	1117	63	144	133	153	253	183
Pr _N	788	18	95	105	103	180	146
LREE _N	2532	104	337	289	336	572	438
Sm _N	945	104	105	162	164	280	214
(Sm / La) _N	1.5	4.6	1.1	3.1	3.4	3.1	1.3
Nd _N	757	24	77	117	106	186	154
Gd _N	1021	335	198	270	346	441	209
Eu _N	393	11	36	60	60	108	98
Ce _N / Ce*	1.7	2.7	1.6	1.9	2.0	2.1	0.5
Eu _N / Eu*	0.40	0.06	0.25	0.29	0.27	0.25	0.10
Yb / Ta	73	253	134	241	135	155	54
Y / Nb	15	181	56	128	78	87	39
Σ REE	4665	2200	1033	1890	2070	2301	629
Y + Σ REE	9279	5624	2512	4646	5122	5501	1325

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Ilha Anchieta (IA-10D)								
Isotope (ppm)	pto1 <i>white rim</i>	pto10 <i>white rim</i>	pto5 <i>black rim</i>	pto17 <i>grey rim</i>	pto8 <i>white rim</i>	pto16 <i>white rim</i>	pto12 <i>rim-core</i>	pto13 <i>white rim</i>
⁷ Li	1.61	9.77	1.09	<1.28	5.38	1.46	<1.05	<1.06
²⁴ Mg	0.62	1.36	<0.65	0.49	17.8	<0.65	0.62	2.00
²⁷ Al	10.2	<2.54	<2.31	<2.72	119	<2.47	<2.35	2.65
²⁹ Si	171113	180849	172288	189685	173807	161274	188716	169042
³¹ P	189	185	289	299	192	158	123	212
⁴⁴ Ca	<267	<267	302	<273	<282	<261	<239	300
⁴⁵ Sc	254	243	221	276	255	241	245	256
⁴⁹ Ti	18.1	10.0	24.0	18.3	15.7	25.3	7.37	23.8
⁵⁵ Mn	<0.97	<0.94	1.2	<1.07	<1.05	<1.00	<0.88	<0.86
⁵⁶ Fe	30.4	<14	17.7	19.7	113	<14	<12	<13
⁸⁵ Rb	<0.212	0.31	<0.19	0.33	0.44	0.32	<0.17	<0.193
⁸⁸ Sr	0.39	0.36	0.56	0.40	0.50	0.32	0.18	0.35
⁸⁹ Y	798	1261	1313	1489	1387	1023	412	991
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	10.7	11.3	11.0	10.3	10.3	10.8	10.7	10.2
⁹⁵ Mo	10.3	10.3	8.44	9.84	11.3	12.2	7.96	10.9
¹³⁷ Ba	0.23	<0.276	<0.41	<0.32	0.75	<0.35	<0.26	<0.23
¹³⁹ La	<0.034	0.593	1.38	0.14	1.04	<0.064	0.036	<0.052
¹⁴⁰ Ce	17.7	28.5	31.8	14.3	36.1	18.3	18.4	16.3
¹⁴¹ Pr	0.18	0.33	0.55	0.60	0.49	0.47	0.08	0.32
¹⁴³ Nd	2.29	3.91	4.22	9.61	6.18	6.71	<0.37	5.53
¹⁴⁷ Sm	4.92	6.94	7.78	12.9	10.28	9.7	1.11	6.34
¹⁵¹ Eu	1.06	1.1	1.31	2.03	2.19	2.15	0.38	1.80
¹⁵⁷ Gd	20.1	34.4	31.2	47.4	39.3	30.7	7.8	26.2
¹⁵⁹ Tb	6.95	10.9	11.9	14.9	13.1	9.43	3.05	8.71
¹⁶³ Dy	72.0	121	127	152	145	97.3	35.3	91.8
¹⁶⁵ Ho	28.1	44.2	46.6	51.2	49.9	33.4	14.5	31.6
¹⁶⁶ Er	119	186	196	207	219	144	67.0	131
¹⁶⁹ Tm	24.7	36.8	37.8	39.4	42.3	27.0	14.9	25.5
¹⁷³ Yb	236	340	339	341	393	260	153	227
¹⁷⁵ Lu	45.4	64.2	61.3	67.6	74.3	53.0	33.6	44.6
¹⁷⁹ Hf	9543	9459	8674	8900	9656	9150	11449	8370
¹⁸¹ Ta	0.65	0.68	0.99	0.75	0.85	1.18	0.92	0.44
²⁰⁷ Pb	2.18	4.51	6.02	2.60	5.34	6.16	3.44	1.47
²⁰⁸ Pb	5.59	10.7	8.72	5.12	10.5	6.86	6.21	3.90
²³² Th	97.4	197	185	108	205	126	91.9	77.9
²³⁸ U	124	190	261	157	228	252	135	66.0
T_{zirc} (°C)	796	741	824	797	782	830	715	823

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Ilha Anchieta (IA-10D)

	pto1	pto10	pto5	pto17	pto8	pto16	pto12	pto13
	<i>white rim</i>	<i>white rim</i>	<i>black rim</i>	<i>grey rim</i>	<i>white rim</i>	<i>white rim</i>	<i>rim-core</i>	<i>white rim</i>
Th / U	0.79	1.04	0.71	0.69	0.90	0.50	0.68	1.18
U / Yb	0.52	0.56	0.77	0.46	0.58	1.0	0.88	0.29
Zr / Hf	52	52	57	56	51	54	43	59
La _N		2.5	5.8	0.58	4.4		0.15	
Ce _N	29	47	52	23	59	30	30	27
Pr _N	1.9	3.5	5.8	6.3	5.1	5.0	0.8	3.4
LREE _N	31	53	64	30	69	35	31	30
Sm _N	32	45	51	84	67	63	7.3	41
(Sm / La) _N		18	8.7	146	15		48	
Nd _N	4.9	8.4	9.0	21	13	14		12
Gd _N	98	167	152	231	191	149	38	127
Eu _N	18	19	23	35	38	37	6.6	31
Ce _N / Ce*		12	7.7	12	9.3			
Eu _N / Eu*	0.33	0.22	0.26	0.25	0.33	0.38	0.40	0.43
Yb / Ta	365	498	343	454	463	220	167	516
Y / Nb	74	112	119	145	135	95	38	97
Σ REE	578	879	898	960	1032	692	349	617
Y+ Σ REE	1376	2140	2212	2449	2419	1715	761	1609

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Ilha Anchieta (IA-10D)							
Isotope (ppm)	pto14b <i>black rim</i>	pto15 <i>grey rim</i>	pto11 <i>black core</i>	pto9 <i>core-rim</i>	Median	Mean	sd
⁷ Li	10.57	2.52	4.54	3.57	3.57	4.50	2.7
²⁴ Mg	5.2	6.4	<0.50	2.33	2.00	4.09	3.8
²⁷ Al	9.79	3.26	<2.53	6.61	8.20	25.4	31.5
²⁹ Si	154307	175886	179578	175195	174501	174312	7340
³¹ P	127	185	170	178	185	192	37
⁴⁴ Ca	<274	<251	<246	<257	301	301	0.8
⁴⁵ Sc	217	250	263	238	247	247	12.3
⁴⁹ Ti	7.74	13.0	7.25	16.3	16.0	15.6	5.4
⁵⁵ Mn	<1.01	<0.96	<0.85	<0.94	1.20	1.20	0.0
⁵⁶ Fe	<14	<13	25.7	<13	25.7	41.2	28.6
⁸⁵ Rb	<0.24	<0.22	0.27	0.33	0.33	0.33	0.0
⁸⁸ Sr	0.21	0.44	0.29	0.36	0.36	0.36	0.1
⁸⁹ Y	726	1173	807	969	1007	1029	246
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	11.2	12.5	12.5	11.8	10.9	11.1	0.6
⁹⁵ Mo	10.6	9.85	8.63	10.6	10.3	10.1	0.9
¹³⁷ Ba	0.31	0.26	<0.40	<0.35	0.29	0.39	0.2
¹³⁹ La	1.78	0.241	<0.043	0.228	0.42	0.68	0.5
¹⁴⁰ Ce	30.3	27.7	26.0	21.7	23.8	23.9	6.1
¹⁴¹ Pr	0.13	0.24	0.09	0.41	0.33	0.32	0.2
¹⁴³ Nd	1.5	3.94	0.67	4.68	4.22	4.48	1.9
¹⁴⁷ Sm	2.3	7.32	2.47	7.9	7.13	6.66	2.7
¹⁵¹ Eu	0.279	1.22	0.237	1.52	1.27	1.27	0.6
¹⁵⁷ Gd	12.2	28.1	17.1	32.1	29.4	27.2	8.8
¹⁵⁹ Tb	4.34	10.4	5.84	10.4	9.91	9.16	2.8
¹⁶³ Dy	55.9	111	76.7	108	103	99.5	28
¹⁶⁵ Ho	21.4	40.1	30.0	36.1	34.8	35.6	9.1
¹⁶⁶ Er	99	174	138	149	146	152	37
¹⁶⁹ Tm	21.9	34.3	29.3	28.0	28.6	30.2	6.6
¹⁷³ Yb	233	323	290	260	275	283	55
¹⁷⁵ Lu	50.1	65.9	55.7	51.0	54.3	55.5	9.3
¹⁷⁹ Hf	10195	10221	12927	9472	9507	9835	909
¹⁸¹ Ta	1.50	1.38	1.79	0.98	0.95	1.01	0.3
²⁰⁷ Pb	8.82	6.31	11.7	5.47	5.41	5.34	2.1
²⁰⁸ Pb	11.97	10.4	12.6	9.04	8.88	8.5	2.4
²³² Th	242	211	232	153	169	160	51
²³⁸ U	436	310	558	236	232	246	98
<i>T_{zirc}</i> (°C)	719	764	713	786	784	774	36

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Ilha Anchieta (IA-10D)

	pto14b	pto15	pto11	pto9	Median	Mean	sd
	black rim	grey rim	black core	core-rim			
Th / U	0.55	0.68	0.42	0.65	0.7	0.7	0.2
U / Yb	1.9	1.0	1.9	0.91	0.8	0.9	0.4
Zr / Hf	49	49	38	52	52	51	4
La _N	7.5	1.0		0.96	1.8	2.9	2.3
Ce _N	50	45	43	35	39	39	10
Pr _N	1.4	2.5	0.9	4.3	3.4	3.4	1.6
LREE _N	58	49	43	41	42	44	12
Sm _N	15	48	16	52	47	44	18
(Sm / La) _N	2.0	47		54	33	42	31
Nd _N	3.2	8.4	1.4	10	9.0	9.6	4.0
Gd _N	59	137	83	156	143	132	43
Eu _N	4.8	21	4.1	26	22	22	10
Ce _N / Ce*	8.8	22		17	12	13	4
Eu _N / Eu*	0.16	0.26	0.11	0.29	0.3	0.3	0.1
Yb / Ta	155	234	162	266	304	320	120
Y / Nb	65	94	65	82	94	93	24
Σ REE	534	827	673	710	701	729	158
Y+ Σ REE	1260	2000	1480	1680	1697	1758	405

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Charnockito Ubatuba								
Isotope (ppm)	pto6-1 <i>grey rim</i>	pto8-1 <i>grey rim</i>	pto7-1 <i>white rim</i>	pto10-1 <i>black rim</i>	pto14-1 <i>white rim</i>	pto2-1 <i>white rim</i>	pto4-1 <i>white rim</i>	pto15-1 <i>white rim</i>
⁷ Li	1.43	3.21	<1.13	1.32	<1.28	1.13	1.19	1.70
²⁴ Mg	<0.41	0.45	<0.56	0.71	0.53	34.16	1.05	<0.57
²⁷ Al	8.14	<2.23	<2.90	<2.60	<2.92	93.3	<2.86	11.6
²⁹ Si	178830	182294	174486	163028	170793	159007	173534	188113
³¹ P	203	203	146	238	224	228	175	275
⁴⁴ Ca	<331	<264	<333	<312	<333	<248	<344	<331
⁴⁵ Sc	237	239	252	227	255	246	223	237
⁴⁹ Ti	3.33	5.46	11.9	7.16	12.0	6.20	4.77	5.28
⁵⁵ Mn	<2.13	2.14	<2.10	<1.93	<1.97	2.5	<2.13	<1.92
⁵⁶ Fe	<19	<15	<19	<16	<16	1037	<16	<16
⁸⁵ Rb	0.344	0.254	0.142	0.553	<0.134	0.79	0.144	0.386
⁸⁸ Sr	0.426	0.349	0.222	0.61	0.343	0.86	0.215	0.335
⁸⁹ Y	799	1124	652	1946	752	2145	660	1201
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	12.6	13.9	11.0	12.0	9.9	12.1	11.4	12.5
⁹⁵ Mo	8.96	10.71	11.19	9.99	11.2	9.4	10.29	9.77
¹³⁷ Ba	<0.210	<0.26	<0.18	0.184	<0.19	0.94	<0.28	<0.23
¹³⁹ La	0.028	0.028	<0.023	0.061	<0.024	0.396	0.0053	0.055
¹⁴⁰ Ce	14.7	17.1	5.66	14.1	4.05	12.8	8.73	15.3
¹⁴¹ Pr	0.09	0.12	0.09	0.38	0.09	0.48	0.05	0.06
¹⁴³ Nd	0.97	2.14	1.48	7.13	2.41	7.1	1.44	2.5
¹⁴⁷ Sm	2.73	2.99	2.68	12.1	4.73	13.3	2.9	5.25
¹⁵¹ Eu	0.251	0.107	0.532	1.04	0.72	1.64	0.24	0.352
¹⁵⁷ Gd	15.7	21.7	14.9	51.8	19.5	57.5	14.0	26.2
¹⁵⁹ Tb	5.69	8.73	5.17	18.1	6.52	19.4	4.79	9.78
¹⁶³ Dy	72.1	103	61.3	199	73.3	223	57.1	117
¹⁶⁵ Ho	27.6	37.9	22.0	69.6	27.2	73.2	22.4	42.4
¹⁶⁶ Er	128	170	98	293	115	321	99	184
¹⁶⁹ Tm	24.7	33.4	20.0	54.5	22.7	61.5	20.2	36.4
¹⁷³ Yb	227	300	181	474	206	558	192	317
¹⁷⁵ Lu	46.5	60.9	37.2	93.2	43.2	111.2	41.1	69.2
¹⁷⁹ Hf	11179	11271	9718	10312	9551	9917	11462	11568
¹⁸¹ Ta	1.14	1.87	0.42	0.84	0.30	0.98	0.96	1.20
²⁰⁷ Pb	6.20	6.90	1.90	12.14	1.31	4.72	2.75	5.79
²⁰⁸ Pb	6.06	7.83	2.17	8.92	1.77	11.01	2.40	8.47
²³² Th	122	150	39.6	187	34.6	202	50.4	146
²³⁸ U	254	300	80	288	60.0	233	107	246
<i>T_{zirc}</i> (°C)	653	690	756	712	757	701	680	688

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Charnockito Ubatuba

	pto6-1 <i>grey rim</i>	pto8-1 <i>grey rim</i>	pto7-1 <i>white rim</i>	pto10-1 <i>black rim</i>	pto14-1 <i>white rim</i>	pto2-1 <i>white rim</i>	pto4-1 <i>white rim</i>	pto15-1 <i>white rim</i>
Th / U	0.48	0.50	0.49	0.65	0.58	0.86	0.47	0.59
U / Yb	1.1	1.0	0.4	0.6	0.3	0.4	0.6	0.8
Zr / Hf	44	44	51	48	52	50	43	43
La _N	0.12	0.12		0.26		1.67	0.02	0.23
Ce _N	24	28	9.2	23	6.6	21	14	25
Pr _N	1.0	1.2	1.0	4.0	1.0	5.0	0.6	0.6
LREE _N	25	29	10	27	8	28	15	26
Sm _N	18	20	18	79	31	87	19	34
(Sm / La) _N	151	165		307		52	848	148
Nd _N	2.1	4.6	3.2	15	5.2	15	3.1	5.4
Gd _N	76	106	72	252	95	280	68	128
Eu _N	4.3	1.8	9.2	18	12	28	4.1	6.1
Ce _N / Ce*	78	70		23		6.0	124	38
Eu _N / Eu*	0.12	0.04	0.26	0.13	0.23	0.18	0.12	0.09
Yb / Ta	199	160	428	564	677	570	200	264
Y / Nb	63	81	59	162	76	177	58	96
Σ REE	566	758	451	1289	525	1460	464	826
Y + Σ REE	1365	1882	1103	3235	1277	3605	1124	2027

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Charnockito Ubatuba							
Isotope (ppm)	pto16-1 <i>white rim</i>	pto17-1 <i>white rim</i>	pto9-1 <i>black rim</i>	pto12-1n <i>black rim</i>	Median	Mean	sd
⁷ Li	1.24	<1.19	1.39	0.89	1.32	1.50	0.4
²⁴ Mg	0.7	<0.60	0.78	1.04	0.75	4.93	7.3
²⁷ Al	<3.26	<3.09	<3.25	3.57	9.85	29.13	32.1
²⁹ Si	183143	180432	184946	185790	179631	177033	7386
³¹ P	230	230	233	236	229	218	24
⁴⁴ Ca	<382	<379	<388	<308			
⁴⁵ Sc	236	234	239	257	238	240	8.0
⁴⁹ Ti	8.68	5.90	8.25	6.39	6.30	7.11	2.07
⁵⁵ Mn	<2.23	<2.20	<2.44	<1.91	2.32	2.32	0.18
⁵⁶ Fe	<18	<18	40.34	<16	539	539	499
⁸⁵ Rb	0.225	0.225	0.195	0.329	0.25	0.33	0.14
⁸⁸ Sr	0.473	0.379	0.481	0.539	0.40	0.44	0.13
⁸⁹ Y	1135	922	1062	1465	1093	1155	356
⁹¹ Zr	496007	496007	496007	496007	496007	496007	
⁹³ Nb	11.2	11.5	13.4	11.4	11.8	11.9	0.8
⁹⁵ Mo	9.97	11.26	11.37	11.38	10.5	10.5	0.7
¹³⁷ Ba	0.091	<0.22	<0.42	<0.301	0.18	0.41	0.36
¹³⁹ La	<0.028	0.022	<0.034	0.051	0.04	0.08	0.08
¹⁴⁰ Ce	8.18	9.37	17.3	10.9	11.8	11.5	3.7
¹⁴¹ Pr	0.13	0.06	0.08	0.22	0.09	0.15	0.10
¹⁴³ Nd	2.65	1.27	2.39	4.44	2.40	2.99	1.62
¹⁴⁷ Sm	6.18	3.17	5.18	7.46	4.96	5.72	2.69
¹⁵¹ Eu	0.75	0.494	0.213	0.67	0.51	0.58	0.32
¹⁵⁷ Gd	30.2	17.5	24.9	35.6	23.3	27.5	10.9
¹⁵⁹ Tb	10.1	6.76	9.26	12.1	9.00	9.71	3.51
¹⁶³ Dy	114	79.0	105	141	104	112	39
¹⁶⁵ Ho	40.7	31.1	38.3	50.8	38.1	40.3	12.6
¹⁶⁶ Er	171	136	170	221	170	176	53
¹⁶⁹ Tm	34.7	27.0	33.2	42.6	33.3	34.2	9.8
¹⁷³ Yb	302	255	297	377	298	307	83
¹⁷⁵ Lu	63.6	54.6	61.5	75.2	61.2	63.1	16.1
¹⁷⁹ Hf	10475	10197	11252	9893	10393	10566	650
¹⁸¹ Ta	0.67	0.75	1.41	1.01	0.97	0.96	0.31
²⁰⁷ Pb	3.23	3.40	6.05	4.70	4.71	4.92	2.08
²⁰⁸ Pb	4.55	4.99	7.24	7.38	6.65	6.07	2.41
²³² Th	81.8	84.4	141	138	130	115	47
²³⁸ U	132	164	247	241	237	196	73
<i>T_{zirc}</i> (°C)	729	697	724	703	702	708	24

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Charnockito Ubatuba

	pto16-1 <i>white rim</i>	pto17-1 <i>white rim</i>	pto9-1 <i>black rim</i>	pto12-1n <i>black rim</i>	Median	Mean	sd
Th / U	0.62	0.51	0.57	0.57	0.6	0.6	0.1
U / Yb	0.4	0.6	0.8	0.6	0.6	0.6	0.2
Zr / Hf	47	49	44	50	48	47	3
La _N		0.09		0.22	0.17	0.34	0.33
Ce _N	13	15	28	18	19	19	6.0
Pr _N	1.3	0.6	0.9	2.3	1.0	1.6	1.1
LREE _N	15	16	29	20	23	21	6.7
Sm _N	40	21	34	49	32	37	18
(Sm / La) _N		223		227	194	265	156
Nd _N	5.7	2.7	5.1	10	5.1	6.4	3.5
Gd _N	147	85	121	173	113	134	53
Eu _N	13	8.5	3.7	12	8.8	10	5.5
Ce _N / Ce*		54		23	46	52	29
Eu _N / Eu*	0.17	0.20	0.06	0.13	0.13	0.14	0.05
Yb / Ta	451	340	210	373	357	370	141
Y / Nb	101	80	80	129	80.3	96.8	30.3
Σ REE	785	621	764	979	761	791	232
Y + Σ REE	1920	1543	1826	2444	1854	1946	588

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipás (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Enclave de Itaquí (ITQ-E)								
Isotope (ppm)	ITQ-E_1 <i>interm</i>	ITQ-E_4 <i>rim</i>	ITQ-E_5 <i>rim</i>	ITQ-E_6 <i>rim</i>	ITQ-E_3 <i>core</i>	ITQ-E_7 <i>core</i>	ITQ-E_9 <i>core</i>	ITQ-E_2 <i>rim</i>
⁷ Li	6.66	12.20	13.99	11.10	8.30	9.71	6.92	17.63
²⁴ Mg	<1.42	<1.35	<1.54	<1.42	<1.54	<1.52	<1.54	<1.62
²⁷ Al	12	5.01	<3.17	<2.94	46.03	7.78	<3.16	3.45
²⁹ Si	173944	180680	174726	193655	176190	176534	165869	188091
³¹ P	<50.64	101	94.6	109	82.3	61.4	<41.63	73.69
⁴⁴ Ca	<283	<209	<292	<272	<282	<253	<256	<283
⁴⁵ Sc	275	303	277	313	282	293	264	296
⁴⁹ Ti	9.68	9.71	<4.63	<4.56	6.15	<3.77	5.48	<4.27
⁵⁵ Mn	<1.50	<1.07	<1.56	<1.37	<1.56	<1.28	<1.27	<1.46
⁵⁶ Fe	<22.87	35.9	<24.05	76.96	<23.73	<21.49	<20.90	105.5
⁸⁵ Rb	0.58	<0.18	<0.23	<0.25	6.19	<0.20	<0.21	0.31
⁸⁸ Sr	0.17	<0.122	0.21	0.19	0.60	0.26	<0.13	0.45
⁸⁹ Y	500	771	728	678	430	378	421	538
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	3.83	4.23	3.84	3.78	3.64	3.42	3.48	3.33
⁹⁵ Mo	3.73	3.43	2.2	3.53	3.42	4.16	1.7	3.13
¹³⁷ Ba	<0.64	<0.40	<0.52	<0.68	0.65	0.74	<0.55	<0.50
¹³⁹ La	5.98	0.39	0.23	0.13	4.78	0.76	0.53	0.13
¹⁴⁰ Ce	62.4	31.4	30.3	22.8	50.5	18.2	16.9	19.3
¹⁴¹ Pr	7.73	0.25	0.28	<0.063	6.44	0.93	0.51	0.25
¹⁴³ Nd	42.8	1.49	2.38	0.61	31.5	7.41	2.68	1.19
¹⁴⁷ Sm	10.1	2.18	1.82	1.27	11.42	2.45	1.36	1.22
¹⁵¹ Eu	3.62	0.44	0.88	0.42	2.72	1.05	0.97	0.66
¹⁵⁷ Gd	11.5	11.6	10.9	6.93	14.2	7.07	8.29	7.66
¹⁵⁹ Tb	3.27	3.11	3.33	2.9	3.5	1.59	2.77	2.61
¹⁶³ Dy	37.8	43.9	51	40.7	33.5	23.9	30.7	35.5
¹⁶⁵ Ho	13.8	18.6	20.9	18.0	13.3	9.9	13.7	15.1
¹⁶⁶ Er	75.3	97.8	122	94.0	66.4	55.1	62.5	80.8
¹⁶⁹ Tm	19.7	23.7	26.9	25.2	15.5	13.2	15.0	19.9
¹⁷³ Yb	224	252	310	283	177	151	170	225
¹⁷⁵ Lu	55.0	68.9	84.9	74.4	46.6	36.7	43.2	61.5
¹⁷⁹ Hf	12724	9888	11590	10729	12507	11282	12737	11259
¹⁸¹ Ta	0.28	0.40	0.42	0.31	0.31	0.16	0.17	0.14
²⁰⁷ Pb	15.6	16.6	20.8	16.1	11.6	11.5	10.3	14.2
²⁰⁸ Pb	11.5	17.6	16.3	12.8	10.8	7.8	7.6	11.4
²³² Th	205	277	250	198	186	116	149	181
²³⁸ U	582	637	707	653	413	370	384	535
<i>T_{zirc}</i> (°C)	738	738			700		691	

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Enclave de Itaqui (ITQ-E)

	ITQ-E_1	ITQ-E_4	ITQ-E_5	ITQ-E_6	ITQ-E_3	ITQ-E_7	ITQ-E_9	ITQ-E_2
	<i>interm</i>	<i>rim</i>	<i>rim</i>	<i>rim</i>	<i>core</i>	<i>core</i>	<i>core</i>	<i>rim</i>
Th / U	0.35	0.43	0.35	0.30	0.45	0.31	0.39	0.34
U / Yb	2.6	2.5	2.3	2.3	2.3	2.4	2.3	2.4
Zr / Hf	39	50	43	46	40	44	39	44
La _N	25	1.6	1.0	0.5	20	3.2	2.2	0.5
Ce _N	102	51	50	37	83	30	28	32
Pr _N	81	2.7	2.9		68	10	5.4	2.6
LREE _N	209	56	53	38	170	43	35	35
Sm _N	66	14	12	8	75	16	8.9	8.0
(Sm / La) _N	2.6	8.7	12	15	3.7	5.0	4.0	15.0
Nd _N	92	3.2	5.1	1.3	67	16	5.7	2.5
Gd _N	56	56	53	34	69	34	40	37
Eu _N	62	8	15	7	47	18	17	11
Ce _N / Ce*	2.6	25	29	51	2.7	5.4	9.0	35
Eu _N / Eu*	1.0	0.3	0.6	0.4	0.7	0.8	0.9	0.7
Yb / Ta	800	631	739	905	570	941	979	1565
Y / Nb	131	182	189	179	118	110	121	161
Σ REE	573	556	666	571	477	330	369	471
Y+ Σ REE	1073	1328	1394	1248	907	707	790	1009

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Enclave de Itaqui (ITQ-E)							
Isotope (ppm)	ITQ-E_8 <i>interm</i>	ITQ-E_10 <i>dark rim</i>	ITQ-E_11 <i>dark rim</i>	ITQ-E_13 <i>dark rim</i>	Median	Mean	sd
⁷ Li	23.5	116	33.9	65.0	13.1	27.0	22.2
²⁴ Mg	3.15	1048	33.7	<2.01	33.7	362	458
²⁷ Al	19.95	6393.07	89.94	83.3	20.0	740	1256
²⁹ Si	205783	263862	203158	188228	184385	190893	17147
³¹ P	98.2	323	492	247	100	168	111
⁴⁴ Ca	<264	1301	5253	436	1301	2330	1949
⁴⁵ Sc	333	431	392	331	299	316	37
⁴⁹ Ti	5.85	60.5	43.2	14.6	9.70	19.4	16.2
⁵⁵ Mn	3.78	53.4	181	3.60	28.6	60.4	60.2
⁵⁶ Fe	359	5131	669	<26.88	232	1063	1356
⁸⁵ Rb	<0.24	34.5	1.49	1.2	1.35	7.38	9.04
⁸⁸ Sr	0.92	26.9	127	1.41	0.52	15.8	24.4
⁸⁹ Y	726	2238	7383	4229	702	1585	1516
⁹¹ Zr	496007	496007	496007	496007	496007	496007	0
⁹³ Nb	5.38	13.2	65.3	28.8	3.84	11.8	11.9
⁹⁵ Mo	2.7	6.7	2.25	2.04	3.28	3.2	0.9
¹³⁷ Ba	<0.47	24.1	24.3	0.86	0.86	10.1	11.3
¹³⁹ La	2.11	16.3	3.26	0.74	0.75	2.9	3.1
¹⁴⁰ Ce	44.4	273	2256	887	37.9	309.4	420.8
¹⁴¹ Pr	0.77	12.9	13.7	4.19	0.9	4.4	4.2
¹⁴³ Nd	4.58	73.3	148	55.5	6.0	31.0	32.7
¹⁴⁷ Sm	1.49	10.3	124	53.5	2.3	18.4	23.4
¹⁵¹ Eu	1.34	4.18	42.7	28.4	1.2	7.3	9.4
¹⁵⁷ Gd	10.9	40.7	346	182	11.2	54.8	69.8
¹⁵⁹ Tb	3.87	12.1	84.6	46.3	3.3	14.2	17.1
¹⁶³ Dy	50.9	178	772	413	42.3	143	156
¹⁶⁵ Ho	21.8	74.7	241	130	18.3	49.2	49.7
¹⁶⁶ Er	110	415	965	518	95.9	222	205
¹⁶⁹ Tm	27.0	98.4	190	96.8	24.4	47.6	40.4
¹⁷³ Yb	288	1029	1705	865	268	473	363
¹⁷⁵ Lu	79.1	253	344	174	71.6	110.1	73.4
¹⁷⁹ Hf	11628	9523	8951	8095	11271	10909	1227
¹⁸¹ Ta	0.47	0.80	5.37	1.78	0.4	0.9	0.9
²⁰⁷ Pb	30.0	146	234	212	16.3	61.5	67.8
²⁰⁸ Pb	22.2	457	2742	2720	14.5	503	743
²³² Th	364	7078	43554	48705	228	8439	12564
²³⁸ U	953	4434	8312	8426	645	2200	2428
<i>T_{zirc}</i> (°C)	696	928	888	775	738	769	71

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02). Terra Nova (TN-1). Cantareira (Cant-6. MD-42B). Itaquí and enclave (ITQ-2. MD-24. ITQ-E). Taipás (TAP-01. TAD-01). Ilha Anchieta (IA-10). Ubatuba charnockite (CHA-1). Tico-Tico (Tico-2). São Roque (SR-07). Itu (ITU-14X). and Perus tourmaline granite (Pe-04).

Enclave de Itaquí (ITQ-E)

	ITQ-E_8 <i>interm</i>	ITQ-E_10 <i>dark rim</i>	ITQ-E_11 <i>dark rim</i>	ITQ-E_13 <i>dark rim</i>	Median	Mean	sd
Th / U	0.38	1.60	5.24	5.78	0.4	1.3	1.4
U / Yb	3.3	4.3	4.9	9.7	2.5	3.4	1.4
Zr / Hf	43	52	55	61	44	46	5.6
La _N	8.9	69	14	3.1	3.2	12	13
Ce _N	73	447	3687	1450	62	506	688
Pr _N	8.1	136	144	44	10	46	45
LREE _N	90	651	3844	1497	73	560	719
Sm _N	10	67	811	349	15	120	153
(Sm / La) _N	1.1	1.0	59	112	6.8	20	22
Nd _N	10	157	317	119	13	66	70
Gd _N	53	198	1684	888	55	267	340
Eu _N	23	72	737	489	21	126	162
Ce _N / Ce*	7.9	4.9	94	138	17	34	31
Eu _N / Eu*	1.0	0.6	0.6	0.9	0.7	0.7	0.2
Yb / Ta	614	1286	317	486	769	819	263
Y / Nb	135	170	113	147	141	146	25
Σ REE	646	2491	7236	3454	572	1487	1453
Y+ Σ REE	1373	4729	14619	7683	1288	3072	2969

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaquí and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Dique de Taipas (TAD-1)								
Isotope (ppm)	TAD-1-1 <i>light rim</i>	TAD-1-2 <i>light rim</i>	TAD-1-4 <i>light rim</i>	TAD-1-5 <i>light rim</i>	TAD-1-6 <i>light rim</i>	TAD-1-9 <i>light rim</i>	TAD-1-10 <i>light rim</i>	TAD-1-11 <i>dark rim</i>
⁷ Li	<1.26	<0.94	<1.91	1.36	4.21	2.17	<1.72	<1.73
²⁴ Mg	<0.63	11.0	12.1	1.9	<0.84	<0.93	6.01	1.03
²⁷ Al	29.3	124	79.9	42.6	85	31.4	83.8	3.59
²⁹ Si	174968	170737	145796	165352	163627	201436	166641	160073
³¹ P	210	85.0	206	169	<41	903	98.9	86.6
⁴⁴ Ca	<270	<276	<344	<260	<283	617	<285	<315
⁴⁵ Sc	276	329	252	291	258	260	403	329
⁴⁹ Ti	4.58	6.07	72.82	19.67	4.56	<3.66	7.88	<3.47
⁵⁵ Mn	1.42	1.65	<1.38	1.93	<1.11	<1.14	<1.17	<1.21
⁵⁶ Fe	<21.85	<21.46	<26.79	<19.26	48.2	140	24.3	<22.01
⁸⁵ Rb	<0.189	<0.171	0.28	0.26	<0.13	0.18	0.37	<0.25
⁸⁸ Sr	1.24	0.34	0.35	0.77	0.35	0.71	0.43	<0.112
⁸⁹ Y	788	635	978	965	104	481	801	524
⁹¹ Zr	496007	496007	496007	496007	496007	496007	496007	496007
⁹³ Nb	5.24	3.39	4.74	4.7	2.18	4.05	3.33	3.9
⁹⁵ Mo	2.28	2.73	<0.79	1.36	1.73	2.25	1.39	2.57
¹³⁷ Ba	0.40	<0.28	<0.50	0.46	<0.43	<0.42	1.30	<0.28
¹³⁹ La	0.35	0.52	0.35	1.42	<0.064	1.84	0.72	0.06
¹⁴⁰ Ce	39.5	20.1	39.3	53.7	6.3	25.5	28.9	18.9
¹⁴¹ Pr	0.30	0.60	0.66	1.95	<0.042	0.39	1.41	0.11
¹⁴³ Nd	2.36	5.89	4.90	12.9	0.41	2.32	13.0	0.84
¹⁴⁷ Sm	3.41	5.97	5.93	9.07	<0.46	2.48	12.9	0.66
¹⁵¹ Eu	2.05	2.75	3.33	4.69	0.16	1.31	4.80	1.23
¹⁵⁷ Gd	22.9	20.5	24.9	33.4	2.89	14.4	31.3	10.0
¹⁵⁹ Tb	7.19	6.08	8.44	9.60	0.63	4.72	7.40	3.46
¹⁶³ Dy	80.3	61.1	91.7	104	4.35	50.7	67.0	43.2
¹⁶⁵ Ho	26.6	21.6	33.4	33.0	2.92	17.6	20.7	16.5
¹⁶⁶ Er	110	95	154	129	11.8	76.6	86.0	78.8
¹⁶⁹ Tm	22.9	19.7	27.1	25.7	3.0	15.2	18.1	16.6
¹⁷³ Yb	208	175	219	221	32.8	145	192	176
¹⁷⁵ Lu	37.5	36.0	40.8	43.6	8.7	26.3	40.5	40.4
¹⁷⁹ Hf	10216	10971	9057	10498	11365	12035	9368	11236
¹⁸¹ Ta	0.74	0.47	0.57	0.59	<0.089	0.85	0.44	0.46
²⁰⁷ Pb	3.90	3.33	5.73	4.44	4.37	2.83	6.57	6.35
²⁰⁸ Pb	8.06	3.76	10.40	9.45	5.49	6.15	8.27	6.19
²³² Th	134	80	164	150	52	104	171	119
²³⁸ U	149	139	142	157	88	144	260	197
<i>T_{zirc}</i> (°C)	677	699	952	804	676		720	

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02). Terra Nova (TN-1). Cantareira (Cant-6. MD-42B). Itaquí and enclave (ITQ-2. MD-24. ITQ-E). Taipás (TAP-01. TAD-01). Ilha Anchieta (IA-10). Ubatuba charnockite (CHA-1). Tico-Tico (Tico-2). São Roque (SR-07). Itu (ITU-14X). and Perus tourmaline granite (Pe-04).

Dique de Taipás (TAD-1)

	TAD-1-1	TAD-1-2	TAD-1-4	TAD-1-5	TAD-1-6	TAD-1-9	TAD-1-10	TAD-1-11
	<i>light rim</i>	<i>light rim</i>	<i>light rim</i>	<i>light rim</i>	<i>light rim</i>	<i>light rim</i>	<i>light rim</i>	<i>dark rim</i>
Th / U	0.90	0.58	1.15	0.95	0.59	0.72	0.66	0.60
U / Yb	0.7	0.8	0.7	0.7	2.7	1.0	1.4	1.1
Zr / Hf	49	45	55	47	44	41	53	44
La _N	1.5	2.2	1.5	6.0		7.8	3.0	0.3
Ce _N	65	33	64	88	10	42	47	31
Pr _N	3.1	6.3	6.9	20.5		4.1	14.8	1.2
LREE _N	69	41	73	114	10	53	65	32
Sm _N	22	39	39	59		16	84	4.3
(Sm / La) _N	15	18	26	10		2	28	16
Nd _N	5.1	13	10	28	0.9	5.0	28	1.8
Gd _N	111	100	121	162	14	70	152	49
Eu _N	35	47	57	81	2.8	23	83	21
Ce _N / Ce*	0.05	0.07	0.03	0.21		0.51	0.07	0.01
Eu _N / Eu*	5.9	4.4	4.4	2.9		4.3	3.6	6.4
Yb / Ta	281	371	383	378		171	436	383
Y / Nb	150	187	206	205	48	119	240	134
Σ REE	563	471	654	684	74	385	524	407
Y+ Σ REE	1352	1105	1632	1648	178	865	1325	931

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02), Terra Nova (TN-1), Cantareira (Cant-6, MD-42B), Itaqui and enclave (ITQ-2, MD-24, ITQ-E), Taipas (TAP-01, TAD-01), Ilha Anchieta (IA-10), Ubatuba charnockite (CHA-1), Tico-Tico (Tico-2), São Roque (SR-07), Itu (ITU-14X), and Perus tourmaline granite (Pe-04).

Dique de Taipas (TAD-1)							
Isotope (ppm)	TAD-1-12 dark rim	TAD-1-13 dark rim	TAD-1-3 dark rim	TAD-1-7 dark rim	Median	Mean	sd
⁷ Li	2.23	<1.17	2.65	4.42	2.44	2.84	1.7
²⁴ Mg	<0.79	<0.90	<0.95	233	8.53	44.2	66.7
²⁷ Al	<2.55	2.04	<2.26	1051	61.3	153	294
²⁹ Si	166636	159090	169524	181930	166639	168818	13576
³¹ P	<46.74	200	178	109	173	224	237
⁴⁴ Ca	<283.77	<233.79	453.88	<250.61	536	536	211
⁴⁵ Sc	269	244	334	342	283	299	48
⁴⁹ Ti	<3.35	7.43	3.65	255	7.43	42.4	73.0
⁵⁵ Mn	<1.13	<0.95	1.44	24.4	1.65	6.18	6.9
⁵⁶ Fe	<20.59	<15.84	88.9	811	88.9	223	231
⁸⁵ Rb	<0.164	0.20	<0.187	3.50	0.27	0.80	1.0
⁸⁸ Sr	0.17	0.13	0.55	2.43	0.43	0.68	0.7
⁸⁹ Y	359	935	381	620	627	631	274
⁹¹ Zr	496007	496007	496007	496007	496007	496007	0
⁹³ Nb	2.83	3.32	3.01	4.56	3.65	3.77	0.9
⁹⁵ Mo	2.44	2.37	2.19	1.72	2.25	2.09	0.8
¹³⁷ Ba	<0.35	<0.35	<0.36	1.32	0.88	0.87	0.5
¹³⁹ La	<0.034	<0.060	0.33	5.30	0.52	1.21	1.5
¹⁴⁰ Ce	13.2	20.3	16.8	63.0	22.9	28.8	17.0
¹⁴¹ Pr	0.07	0.22	0.08	8.98	0.39	1.34	2.5
¹⁴³ Nd	0.77	3.93	1.51	80.7	3.15	10.8	22.4
¹⁴⁷ Sm	1.49	6.13	1.53	40.8	5.93	8.22	11.1
¹⁵¹ Eu	0.45	2.88	0.73	16.6	2.40	3.41	4.4
¹⁵⁷ Gd	7.25	24.7	7.16	47.7	21.7	20.6	13.0
¹⁵⁹ Tb	2.49	7.77	2.91	8.56	6.64	5.77	2.9
¹⁶³ Dy	29.2	85.5	31.9	64.2	62.6	59.5	29.1
¹⁶⁵ Ho	11.2	28.0	11.5	20.1	20.4	20.3	9.1
¹⁶⁶ Er	50.4	120	57	85.2	85.6	87.8	38.3
¹⁶⁹ Tm	11.9	25.3	12.5	18.8	18.4	18.1	6.9
¹⁷³ Yb	112	244	127	178	177	169	58
¹⁷⁵ Lu	23.2	46.5	27.5	36.1	36.8	33.9	10.7
¹⁷⁹ Hf	10798	8910	10828	10845	10813	10511	961
¹⁸¹ Ta	0.30	0.41	0.19	0.50	0.47	0.50	0.2
²⁰⁷ Pb	2.62	1.84	4.97	6.94	4.41	4.49	1.7
²⁰⁸ Pb	2.96	4.31	8.46	7.59	6.89	6.76	2.3
²³² Th	57	84	148	121	120	115	40
²³⁸ U	121	82	218	232	147	161	55
T_{zirc}(°C)		716	660	1137	716	782	161

Table 2. Obtained values (in ppm) for major, minor and trace elements by LA-ICPMS to the zircons samples: Itaquera (ITA-02). Terra Nova (TN-1). Cantareira (Cant-6. MD-42B). Itaquí and enclave (ITQ-2. MD-24. ITQ-E). Taipás (TAP-01. TAD-01). Ilha Anchieta (IA-10). Ubatuba charnockite (CHA-1). Tico-Tico (Tico-2). São Roque (SR-07). Itu (ITU-14X). and Perus tourmaline granite (Pe-04).

Dique de Taipás (TAD-1)

	TAD-1-12 dark rim	TAD-1-13 dark rim	TAD-1-3 dark rim	TAD-1-7 dark rim	Median	Mean	sd
Th / U	0.47	1.02	0.68	0.52	0.7	0.7	0.2
U / Yb	1.1	0.3	1.7	1.3	1.0	1.1	0.6
Zr / Hf	46	56	46	46	46	48	5
La _N			1.4	22.4	2.2	5.1	6.9
Ce _N	22	33	27	103	37	47	28
Pr _N	0.7	2.3	0.8	94.5	4	14	27
LREE _N	22	36	30	220	47	64	57
Sm _N	10	40	10	267	39	54	75
(Sm / La) _N			7.1	12	15	15	8
Nd _N	1.6	8.4	3.2	173	6.7	23	48
Gd _N	35	120	35	232	105	100	63
Eu _N	7.8	50	13	285	41	59	76
Ce _N / Ce*			0.06	0.76	0.07	0.20	0.26
Eu _N / Eu*	5.8	6.9	3.6	1.2	4.4	4.5	1.7
Yb / Ta	369	602	685	355	378.4	401	139
Y / Nb	127	282	126	136	143.2	163	63
Σ REE	263	616	298	674	497.5	468	189
Y+ Σ REE	622	1551	679	1294	1199.8	1099	455

ELECTRONIC SUPPLEMENTARY FIGURES

Cant-6

ITQ-2

Figure 30. Cathodoluminescence (CL) images of zircon mounts from sixteen different studied samples. For comments. see text.

MD-24 (1^a. part)

MD-24 (2^a. part)

Figure 30. Cathodoluminescence (CL) images of zircon mounts from sixteen different studied samples. For comments. see text.

TAP-1

SR-07

Figure 30. Cathodoluminescence (CL) images of zircon mounts from sixteen different studied samples. For comments. see text.

Tico-2

ITA-2

Figure 30. Cathodoluminescence (CL) images of zircon mounts from sixteen different studied samples. For comments. see text.

CHA-1

MD-42B

Figure 30. Cathodoluminescence (CL) images of zircon mounts from sixteen different studied samples. For comments. see text.

ITQ-E

TAD-1

Figure 30. Cathodoluminescence (CL) of zircon mounts from sixteen different studied samples. For comments, see text.

Figure 30. Cathodoluminescence (CL) of zircon mounts from sixteen different studied samples. For comments. see text.

ITU-14X

IA-10D

Figure 30. Cathodoluminescence (CL) of zircon mounts from sixteen different studied samples. For comments, see text.

ANEXO B

Methodology for the Determination of Trace and Minor Elements in Minerals and Fused Rock Glasses with Laser Ablation Associated with Quadrupole Inductively Coupled Plasma Mass Spectrometry (LA-Q-ICPMS)

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Abstract

The laser ablation technique, coupled with the use of quadrupole ICPMS equipment, proved a powerful tool for determination of trace elements in minerals. At the University of São Paulo, the technique was implemented for the study of minerals such as olivines, pyroxenes and biotites. The main problem to be tackled is the availability of proper multi-element reference materials usually prepared synthetically as glasses with various compositions by NIST and fused rock glasses by the Max Planck Institute (MPI) and USGS (basalts, andesite, quartz diorite, komatiites). The best tested ones are the NIST glasses, with good homogeneity and reliable compositional data for over 40 elements. Results are here presented that test additional RM's. NIST 612 and 610 were used for calibration purposes. The best results were obtained for rock glasses USGS basalts BHVO-2G, BIR-1G and BCR-2G (better homogeneity and recommended values). Our contribution tests especially the MPI komatiites glasses GOR-128 and GOR-132G, basalts KL-2G and ML-3BG, andesite StHs-6/80G and quartz diorite T-1G, discussing homogeneity issues and providing new data. There is a need for additional preparation of reliable reference materials.

Keywords

Laser Ablation, Mass Spectrometry, Geological Reference Materials, Fused Rock Glasses

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1. Introduction

Inductively coupled plasma mass spectrometry, hyphenated with laser ablation (LA-ICPMS), represents an important tool for the direct chemical analyses in solid phases. The main advantage is the possibility of determining the composition even in substances with a complex matrix, as usually present in geologic and environmental materials, semi-conductors, and others. The technique has the advantage of high sensitivity, a wide range of linear intensity responses, and requiring little surface preparation, without presenting major problems with contamination issues. The obtained results can be expressed as either elemental or isotopic proportions and the spatial resolution is of the order of 10 to 300 μm and depth resolution is about 60 nm per pulse [1].

Mass spectrometers can isolate ions with a positive charge effectively by their mass/charge relations. Three types of equipments are available, each one with its own advantages and shortcomings, the quadrupole setting, the time-of-flight performance and the high-resolution sector arrangement.

The quadrupole mass spectrometer setting is the most cost-effective, and hence has become the preferred instrument in many laboratories. The equipment generates voltage intervals and radiofrequencies that can stabilize a definite ion within the quadrupole rods and guide it towards the detector window. Given a predefined setting, ions with a different mass-to-charge ratio will become unstable and be eliminated within the vacuum system. All the desired spectra of ionic masses can be quickly scanned within the quadrupole. Although this analyzer works in a sequential fashion, it can separate efficiently more than 5000 atomic mass units (amu) per second [2].

Therefore, Q-ICPMS equipments associated with laser ablation can perform very fast multi-element determinations of over 40 elements, with sensitivities of the order of $\text{ng}\cdot\text{g}^{-1}$ in any mineral phase, or of materials hidden within them, such as fluid inclusions, in a time-span that does not exceed 1 or 2 minutes of operation.

These techniques opened up new fields of research in igneous petrology, mineralogy and geochronology, determining the distribution of trace elements in several phases (both solid as well as liquid), and enabling also the calculation of the corresponding partition coefficients between mineral pairs, or mineral phases and melts [3] [4].

The main drawback of the quadrupole setting associated with LA is the possibility of isotopic fractionation during analysis, a subject widely discussed in the literature [5] [6], as well as the lack of adequate Certified Reference Materials (CRM) for most of the analyzed minerals, a deficiency that may be corrected with the preparation of new homogeneous synthetic materials [7]. Many such multi-elementary synthetic or natural materials are already available, such as the well-certified NIST 610 and 612 glasses and the synthetic materials prepared by melting of rock powders [8] [9]. The NIST RM's are synthetic glasses with around 40 elements, present in amounts close to $30\text{ mg}\cdot\text{kg}^{-1}$ in the 612 sample, and up to $500\text{ mg}\cdot\text{kg}^{-1}$ in the 610 material. They were used in this contribution as calibration materials. The USGS substances, widely considered the best RM's, are the basaltic glasses BHVO-2G, BIR-1G and BCR-2G, already subjected to many determinations. The Max Planck Institute prepared several additional glassy RM's, such as the komatiites GOR-128 and GOR-132G, the basalts KL-2G and ML-3BG, the andesite StHs-6/80G and the quartz diorite T-1G, still to be tested, as far as certified values and homogeneity is concerned.

The implementation of this methodology at our laboratory started with the handling and analytical determinations using NIST materials for calibration, followed by analytical determinations of the USGS synthetic basaltic glasses (BHVO-2G, BIR-1G and BCR-2G) [8], and, additionally, of the substances offered by the Max Planck Institute [10]. The results obtained for these reference materials during the last 4 years of analytical determinations in our laboratory (where these materials were also analyzed as unknown substances) are here presented and discussed.

2. Analytical Methodology

The indications given in [11] were used as a basis for the implementation of the analytical methodology for trace element determinations in minerals in thin section and in reference materials with the LA-Q-ICPMS methodology.

Mean analytical time spent for analyzing up to 44 elements was 120 s (60 s for reading a blank, 60 s for preparing the instrument and reading results from the analyzed sample). Intensities in cps are calculated as concentrations in real time by the Glitter[®] software (developed by the GEMOC program, Geochemical Evolution and Metallogeny of Continents, Macquarie University, Australia) [12].

Our results were obtained from the determination of the before-mentioned RM's (USGS basalt glasses

BHVO-2G, BIR-1G and BCR-2G; Max Planck's komatiites GOR-128 and GOR-132G, basalts KL02G and ML03BG, quartz diorite T-1G, andesite StHs-6/80G). The obtained results were processed with the Glitter® software [12] for drift correction with the use of an internal standard, together with a check on background, spectral signs and analytical quality, and finished with the calculation of results in weight units. Instrumental parameters are listed in Table 1, and data on the analytical performance are quoted in Table 2 and Table 3.

The analyzed elements and their masses (cited in Table 3) were determined with a dwell time of 8.3ms and integration time of 1660 ms; total time of analysis was 120 s, the first 60 s measuring the background gas fluxes (Helium, He and Argon, Ar) reaching the plasma after passing through the sample cell, followed by 60 s devoted to data acquisition of the materials removed from the laser spot.

The sequence for data acquisition is as follows:

Nist-612 (a), Nist-612 (b), sample (1), ..., sample (6), Nist-612 (c), Nist-612 (d), sample (7), ..., sample (14), Nist-612 (e), Nist-612 (f).

Cleaning was performed after each sample analysis for about 2 minutes with He fluxes, a procedure that stabilizes rapidly the background values, more so than an alternative method, such as obtained with the use of Argon gas. Readings from Nist-612 (a, b, c, d, e, f) were used as an internal standard and for drift correction during the entire 1-hour analytical work. The entire procedure lasts about 3 hours, counting also laser and plasma stabilization times at the beginning of the determinations.

Isotopic interferences occurring during analysis, such as the ones due to $^{28}\text{Si}^{17}\text{O}^+$, $^{27}\text{Al}^{18}\text{O}^+$, $^{90}\text{Zr}^{2+}$ on $^{45}\text{Sc}^+$; $^{43}\text{Ca}^{16}\text{O}^+$ on $^{59}\text{Co}^+$; $^{44}\text{Ca}^{16}\text{O}^+$ on ^{60}Ni ; $^{135}\text{Ba}^{16}\text{O}^+$ on ^{151}Eu , and several others, can however be ignored, since they are usually very limited in dry plasmas, with hydroxyl and oxygen absent. The daily rate of generation of oxide was controlled holding ThO^+ formation lower than 1%. The formation of double-charged species, such as Ba^{2+} , was kept to a maximum of 3%, controlling the gas fluxes.

Table 1. Instrumental parameters used in analytical routine for determination of trace elements by LA-Q-ICPMS.

ICP-MS	Elan-6100DRC	Laser Ablation	Laser New Wave UP-213
RF power	1300 W	Type	Nd:YAG
Auxiliary gas flux (Ar)	1.0 L/min	Wavelength	213 nm
Plasma gas flux (Ar)	16 L/min	Pulse duration	5 ns
Sample cell	Super cell	Laser repeat rate	10 Hz
Carrier gas flux	Ar = 0.58 L/min, He = 0.60 L/min		
Distance to sample	4 mm		
Pt Sampler dimension	1.1 mm		
Pt Skimmer dimension	0.9 mm		
Ionic lens voltage	5.5 to 8.5 V		
Energy density	65% laser power $\sim 8.60 \text{ J/cm}^2$ and 0.2 mJ (spot 65 μm) for pyroxenes, amphiboles		
Energy density	70% laser power $\sim 7 - 10 \text{ J/cm}^2$ and 0.2 - 0.3 mJ (raster with spot of 65 μm) Ablation speed 5 $\mu\text{m/s}$, line of 300 μm for quartz, alkali feldspars		

Table 2. Time parameters and signal processing used for determinations of trace elements.

ICP-Q-MS	Parameters	ICP-Q-MS	Parameters
Sweeps/reading	1	Number of replicates	1
Readings/replicates	270	Settling time	2 ms
Scan mode	Peak hopping	MCA channel	1
Detector	Analogic pulse	Units	Cps
Auto-lens	ON	Mode	Standard (without DRC)

Table 3. Analyzed elements and their isotope masses (time parameters of signal integration, see text).

Element	Mass (u.m.a)	Element	Mass (u.m.a)
Li	7	Sn	118
Be	9	Sb	121
Mg	25	Cs	133
Si	29	Ba	137
P	31	La	139
Ca	42	Ce	140
Sc	45	Pr	141
Ti	49	Nd	143
V	51	Sm	147
Cr	52	Eu	151
Mn	55	Gd	155
Co	59	Tb	159
Ni	60	Dy	163
Cu	65	Ho	165
Zn	66	Er	166
Ga	71	Tm	169
Rb	85	Yb	173
Sr	88	Lu	175
Y	89	Hf	179
Zr	90	Ta	181
Nb	93	Pb	208
Mo	95	Th	232
		U	238

Determination of elemental concentrations can be achieved by means of any of the three cited methods:

- 1) Entirely by external calibration with a solid reference material;
- 2) External calibration with a solid reference material coupled with internal standardization;
- 3) Calibration using solutions.

In our laboratory, the second type of calibration was implemented. The external reference material was used simultaneously with an internal standard. This procedure represents a more robust calibration method, since a correction can be applied on the ablation yield of the sample (the mass of removed material) and the external reference material. The methodology is especially adapted for use with the Glitter[®] software [13]. In addition, matrix effects and signal drift can also be corrected. In practical terms, the internal standard is represented by a major constituent found in known concentrations both in the sample and the reference material. Calcium, in particular, has proven to be an excellent internal standard for many minerals and the NIST glasses. The three minor isotopes of the element (42, 43, 44) can be used better for calibration purposes, since their ablation behavior is similar to the one shown by petrogenetically important minor elements (e.g., REE). For correction purposes, it is assumed that the signal drift occurs linearly with time and at a similar rate for all isotopic masses. When Ca is present in concentrations below 1%, other elements can be used as internal standard, such as Mg or even Si.

The concentration of elements, even though calculated directly with the Glitter[®] software [12], can also be obtained by defining the intensity integration points for background and the sample analyzed by laser, using the

Equation (1):

$$C_{AN_{sample}} = \frac{I_{AN_{sample}}}{S} \quad (1)$$

where:

$C_{AN_{sample}}$ is the concentration of the analyzed element in the sample,

$I_{AN_{sample}}$ is the intensity in cps of the element in the sample and S is the normalized sensitivity, given by Equation (2):

$$S = \frac{I_{AN_{reference}}}{C_{AN_{reference}}} \left(\frac{I_{SI_{sample}}}{I_{SI_{reference}}} \times \frac{C_{SI_{reference}}}{C_{SI_{sample}}} \right) \quad (2)$$

where:

$I_{AN_{reference}}$ is the intensity in cps of the element in the reference material,

$C_{AN_{reference}}$ is the concentration of the element in the reference material,

$I_{SI_{sample}}$ and $I_{SI_{reference}}$ are the intensities in cps of the internal standard (Ca) in the sample and reference material, respectively,

$C_{SI_{sample}}$ and $C_{SI_{reference}}$ are the concentrations of the internal standard (Ca) in the sample and reference material, respectively.

Calculation of this detection limit was defined [13] by Equation (3), below:

$$DL = \frac{3\sigma_{BCG}}{S \times Y} \times \sqrt{\frac{1}{N_{BCG}} + \frac{1}{N_{PK}}} \quad (3)$$

where σ_{BCG} is the standard deviation of replicate analysis of the pre-ablation background identification; N_{BCG} and N_{PK} are the number of replicate determinations used for background and peak signal integration, respectively; S is the normalized sensitivity in cps per unit of concentration for the reference material (see Equation (1)); Y the ablation yield relative to the reference material, determined from the counting intensity measurement and the known concentration of the internal standard.

Detection limits of about tens of $\text{ng}\cdot\text{g}^{-1}$ are expected for present-day instruments, for a moderate spatial peak resolution between 30 to 40 μm . Higher spatial resolutions (of the order of 10 μm) will present detection limits at the $\text{mg}\cdot\text{kg}^{-1}$ range, lower resolutions ($>100 \mu\text{m}$) at a sub- $\text{ng}\cdot\text{g}^{-1}$ range.

Detection limits are calculated for each element in each sample directly by the Glitter® software (cf. Equation (3) [13]). In Table 4 are presented average values and standard deviations of detection limits obtained for elements in several analytical runs.

3. Obtained Results

Data obtained during the last 4 years in our laboratory for USGS basaltic glasses BCR-2G, BIR-1G and BHVO-2G are listed in Tables 5-7. These RM's were used as quality control standards with 30 to 60 obtained values for each analyzed element. Reference values for LA-ICPMS are quoted in [11] and in [10]. In the GEOREM site [14] preferred values are also listed with a mention of the used analytical technique.

Data obtained for the Max Planck Institute basaltic glasses KL-2G and ML-3BG, andesite StHs-6/80G, quartz diorite T-1G and komatiites GOR-128 and GOR-132G are quoted in Tables 8-13 (six to twelve determinations for each material).

Data obtained for materials BHVO-2G, BCR-2G and BIR-1G were calibrated against the synthetic glasses Nist-610 or 612, while the RM from the Max Planck Institute were calibrated exclusively against Nist-612.

4. Discussion of Results

The obtained values for the analyzed elements (Tables 5-7) in the basaltic glasses BHVO-2G, BCR-2G and BIR-1G are represented in graphical form in Figure 1, with variations found in analytical results obtained in

Table 4. Mean detection limits ($\text{mg}\cdot\text{kg}^{-1}$) and standard deviations (sd) obtained in several analytical runs.

Isotope	DL	sd	Isotope	DL	sd	Isotope	DL	sd
^7Li	0.53	0.101	^{88}Sr	0.05	0.008	^{159}Tb	0.03	0.003
^9Be	3.05	0.264	^{89}Y	0.04	0.007	^{163}Dy	0.12	0.011
^{25}Mg	1.40	0.267	^{90}Zr	0.07	0.014	^{165}Ho	0.03	0.004
^{31}P	19.74	2.973	^{93}Nb	0.05	0.006	^{166}Er	0.09	0.015
^{42}Ca	0.03	0.011	^{95}Mo	0.38	0.053	^{169}Tm	0.03	0.002
^{45}Sc	0.60	0.079	^{118}Sn	0.70	0.081	^{173}Yb	0.17	0.034
^{49}Ti	2.09	0.182	^{121}Sb	0.13	0.018	^{175}Lu	0.03	0.005
^{51}V	0.45	0.089	^{133}Cs	0.04	0.005	^{179}Hf	0.20	0.012
^{52}Cr	2.43	0.202	^{137}Ba	0.27	0.050	^{181}Ta	0.03	0.004
^{55}Mn	0.61	0.281	^{139}La	0.04	0.005	^{208}Pb	0.09	0.009
^{59}Co	0.11	0.018	^{140}Ce	0.03	0.007	^{232}Th	0.03	0.001
^{60}Ni	0.52	0.085	^{141}Pr	0.03	0.004	^{238}U	0.03	0.004
^{65}Cu	0.55	0.052	^{143}Nd	0.23	0.031			
^{66}Zn	1.43	0.313	^{147}Sm	0.19	0.031			
^{71}Ga	0.19	0.056	^{151}Eu	0.06	0.009			
^{85}Rb	0.11	0.020	^{155}Gd	0.24	0.050

Figure 1. Relationship between average values and recommended values [11], determined with the LA-Q-ICPMS technique for the analyzed elements in the BCR-2G, BHVO-2G and BIR-1G basaltic glasses (cf. Tables 5-7).

relation to the preferred mean, taking as mean values the ones quoted in [11], determined with the LA-Q-ICPMS technique. Variation diagrams for REE normalized with respect to values of C1 chondrite ([16] and [17]), are presented in Figure 2.

Most obtained values for the referred glasses lie within an interval of $\pm 15\%$ of the reference values of the cited elements, as determined by the LA-Q-ICPMS technique in [11]. The data in Figure 2 also indicate a general compliance with the published contents for the REE elements in three reference materials. Beryllium, uranium and Mo for the BIR-1G and P for BCR-2G are the elements showing the highest deviation from the recommended values.

Table 5. Obtained values in $\text{mg}\cdot\text{kg}^{-1}$ for BCR-2G, compared with values quoted in [11] (LA-ICPMS technique) and preferred values in [14].

Element	Obtained values			Gao <i>et al.</i> [11]			GEOREM [14]	
	Mean	sd	n	Mean	sd	n	Recom**	sd**
Li	9.37	0.52	33	9.9	0.7	67	9	1
Be	2.30	1.10	25	2	0.1	7	2.3	0.4
Mg	21184	1806	43	20980	607	94	21470	1492
P	1334	194	22	<i>n.d</i>			1615	44
Sc	32.0	3.8	41	32	2	132	33	2
Ti	13080	1182	43	13005	1081	124	14100	1000
V	421	11	33	425	7	98	425	18
Cr	17.0	1.3	39	17	2	91	17	2
Mn	1482	34	40	1463	23	10	1550	70
Co	37.2	1.8	39	38	1	118	38	2
Ni	12.2	0.8	29	12.7	0.9	126	13	2
Cu	17.1	1.1	35	18	1	78	21	5
Zn	146	8	38	153	9	14	125	5
Ga	22.7	1.1	38	24	1	71	23	1
Rb	48.5	2.3	39	51	3	133	47	0.5
Sr	326	12	39	321	6	122	342	4
Y	31.6	5.5	38	31	2	138	35	3
Zr	172	20	32	167	8	127	184	15
Nb	11.1	0.8	42	10.9	0.6	133	12.5	1
Mo	237	10	42	<i>n.d</i>			270	30
Sn	2.67	0.46	36	2.4	0.4	14	2.6	0.4
Sb	0.34	0.06	25	0.51	0.87	10	0.35	0.08
Cs	1.18	0.07	34	1.17	0.08	71	1.16	0.07
Ba	647	21	34	641	14	125	683	7
La	25.1	1.4	42	25	1	144	24.7	0.3
Ce	51.5	1.8	41	52	2	139	53.3	0.5
Pr	6.37	0.36	41	6.3	0.4	140	6.7	0.4
Nd	27.6	2.1	42	27	1	132	28.9	0.3
Sm	6.31	0.57	38	6.3	0.5	115	6.59	0.07
Eu	1.95	0.12	37	1.91	0.09	108	1.97	0.02
Gd	6.32	0.81	32	6.5	0.6	112	6.71	0.07
Tb	0.96	0.11	37	0.95	0.07	115	1.02	0.08
Dy	5.92	0.73	37	6	0.4	106	6.44	0.06
Ho	1.21	0.15	35	1.2	0.07	104	1.27	0.08
Er	3.29	0.45	29	3.3	0.2	94	3.7	0.04
Tm	0.47	0.07	33	0.46	0.04	111	0.51	0.04
Yb	3.38	0.28	30	3.2	0.3	112	3.39	0.03
Lu	0.48	0.06	35	0.47	0.04	109	0.503	0.005
Hf	4.47	0.61	36	4.5	0.4	94	4.84	0.28
Ta	0.62	0.08	36	0.63	0.06	97	0.78	0.06
Pb	10.1	0.5	36	10.9	0.5	104	11	1
Th	5.66	0.38	36	5.5	0.2	103	5.9	0.3
U	1.69	0.09	35	1.7	0.08	120	1.69	0.12

** Mean values obtained with various techniques (ID-TIMS, MC-LAICPMS, EPMA, LA-ICPMS). n: number of determinations; Recom: recommended values; *n.d*: not determined.

Table 6. Obtained values in $\text{mg}\cdot\text{kg}^{-1}$ for BIR-1G, compared with values quoted in [11] (LA-ICPMS technique) and preferred values in [14].

Element	Obtained values			Gao <i>et al.</i> [11]			GEOREM [14]	
	Mean	sd	n	Mean	sd	n	Recom**	sd**
Li	3.28	0.36	38	3.6	0.4	57	3	0.7
Be	0.44	0.15	13	0.69	0.88	9	0.1	
Mg	60101	6839	38	58471	1517	65	56400	600
P	109	6	21	<i>n.d</i>			118	13
Sc	38.9	2.6	44	41	1	95	43	3
Ti	5786	598	37	5532	323	97	5400	200
V	330	11	39	338	6	91	326	32
Cr	394	13	40	403	11	85	392	24
Mn	1341	56	44	1417	30	17	1472	77
Co	54.2	2.0	37	57	1	78	52	5
Ni	176	8	40	190	6	85	178	18
Cu	124	4	35	132	6	69	119	12
Zn	77.6	4.9	39	86	5	25	78	17
Ga	16.0	0.7	37	17	1	76	15	2
Rb	0.22	0.03	33	0.26	0.05	68	0.197	0.007
Sr	106	4	41	104	2	102	109	2
Y	12.2	1.0	36	13.3	0.6	99	14.3	1.4
Zr	12.0	1.2	36	12.9	0.6	98	14	1.2
Nb	0.51	0.05	40	0.48	0.04	94	0.52	0.04
Mo	0.089	0.03	23	<i>n.d</i>			0.075	0.011
Sn	1.27	0.26	41	0.84	0.23	9	2.3	1.3
Sb	0.55	0.15	39	0.47	0.13	12	0.56	0.09
Cs	0.011	0.004	21	0.0069	0.0020	31	0.007	0.002
Ba	6.31	0.44	40	6.3	0.3	99	6.5	0.07
La	0.59	0.05	43	0.60	0.04	91	0.609	0.02
Ce	1.92	0.12	45	1.9	0.08	76	1.89	0.04
Pr	0.36	0.04	46	0.36	0.02	78	0.37	0.02
Nd	2.29	0.20	42	2.3	0.2	73	2.37	0.03
Sm	1.06	0.11	37	1.1	0.1	72	1.09	0.02
Eu	0.52	0.05	39	0.51	0.04	78	0.517	0.005
Gd	1.59	0.17	33	1.6	0.1	76	1.85	0.02
Tb	0.31	0.04	30	0.32	0.03	81	0.35	0.04
Dy	2.19	0.21	32	2.3	0.2	78	2.55	0.02
Ho	0.50	0.06	30	0.51	0.05	86	0.56	0.03
Er	1.44	0.10	26	1.5	0.1	80	1.7	0.02
Tm	0.21	0.02	35	0.22	0.02	69	0.24	0.03
Yb	1.46	0.17	34	1.5	0.1	80	1.64	0.03
Lu	0.22	0.02	27	0.23	0.02	63	0.248	0.009
Hf	0.49	0.10	28	0.53	0.06	71	0.57	0.03
Ta	0.03	0.01	40	0.032	0.01	80	0.036	0.006
Pb	3.36	0.21	31	3.6	0.2	78	3.7	0.3
Th	0.03	0.01	44	0.028	0.01	65	0.03	0.002
U	0.02	0.01	31	0.032	0.01	67	0.023	0.006

** Mean values obtained with various techniques (ID-TIMS, MC-LAICPMS, EPMA, LA-ICPMS). n: number of determinations; Recom: recommended values; *n.d*: not determined.

Table 7. Obtained values in $\text{mg}\cdot\text{kg}^{-1}$ for BHVO-2G, compared with values quoted in [11] (LA-ICPMS technique) and preferred values in [14].

Element	Obtained values			Gao <i>et al.</i> [11]			GEOREM [14]	
	Mean	sd	n	Mean	sd	n	Recom**	sd**
Li	4.67	0.42	65	5.0	0.4	26	4.4	0.8
Be	1.24	0.36	40	1.4	0.2	6	1.3	0.2
Mg	45594	4910	51	42682	1071	25	42992	121
P	1281	126	40				1266	87
Sc	29.6	2.1	72	31	1	51	33	2
Ti	16165	1249	39	15621	453	53	16300	900
V	319	9	64	329	9	42	308	19
Cr	288	9	67	285	14	51	293	12
Mn	1310	58	74	1345	25	22	1317	233
Co	45.2	2.1	70	47	2	53	44	2
Ni	120	7	70	112	9	48	116	7
Cu	120	7	72	142	10	52	127	11
Zn	114	6	72	107	26	36	102	6
Ga	21.7	0.8	71	21	1	44	22	3
Rb	9.43	0.53	69	10.1	0.6	49	9.2	0.04
Sr	388	16	72	328	10	53	396	1
Y	22.1	1.6	45	23	1	57	26	2
Zr	155	11	49	160	8	56	170	7
Nb	16.9	1.2	55	16.4	0.7	56	18.3	0.8
Mo	4.09	0.29	62	<i>n.d.</i>			3.8	0.2
Sn	2.06	0.17	58	2.6	0.6	22	2.6	0.6
Sb	0.24	0.07	35	0.21	0.04	10	0.3	0.13
Cs	0.10	0.01	65	0.11	0.02	29	0.1	0.02
Ba	129	7	71	128	4	56	131	2
La	15.2	0.9	63	15.6	0.6	38	15.2	0.2
Ce	37.5	1.4	71	37	1	32	37.6	0.2
Pr	5.08	0.22	68	5.0	0.3	33	5.35	0.22
Nd	23.5	1.3	67	24	1	32	24.5	0.2
Sm	5.75	0.35	59	5.8	0.5	32	6.1	0.03
Eu	2.01	0.11	67	2.0	0.1	28	2.07	0.01
Gd	5.50	0.34	51	5.9	0.4	30	6.16	0.05
Tb	0.85	0.06	40	0.86	0.06	31	0.92	0.04
Dy	4.92	0.38	46	4.9	0.4	33	5.28	0.05
Ho	0.91	0.07	45	0.91	0.06	32	0.98	0.04
Er	2.28	0.18	39	2.3	0.2	28	2.56	0.02
Tm	0.29	0.04	56	0.30	0.05	32	0.34	0.02
Yb	1.96	0.17	41	2.0	0.2	30	2.01	0.02
Lu	0.25	0.03	51	0.26	0.04	29	0.279	0.003
Hf	4.02	0.31	43	4.1	0.4	52	4.32	0.18
Ta	0.96	0.08	54	0.94	0.07	54	1.15	0.1
Pb	1.80	0.13	63	1.4	0.2	43	1.7	0.2
Th	1.15	0.08	53	1.18	0.09	48	1.22	0.05
U	0.45	0.04	56	0.44	0.03	42	0.403	0.003

** Mean values obtained with various techniques (ID-TIMS, MC-LAICPMS, EPMA, LA-ICPMS). n: number of determinations; Recom: recommended values; *n.d.*: not determined.

Table 8. Obtained values in $\text{mg}\cdot\text{kg}^{-1}$ for 12 determinations of basalt glass KL-2G, compared with values quoted in [15].

Elements	Obtained values			Jochum <i>et al.</i> [15]		
	Mean	sd	% rsd	Mean	U	% var.
Li	5.35	0.48	8.9	5.10	0.50	9.8
Sc	29.7	1.2	4.0	31.8	0.90	2.8
Ti	16079	1279	8.0	15347	540	3.5
V	294	14	4.7	309	38	12.3
Cr	283	6	2.1	294	27	9.2
Mn	1190	53	4.5	1278	70	5.5
Co	39.4	1.1	2.7	41.2	2.3	5.6
Ni	101	5.0	4.9	112	5	4.5
Cu	81.6	3.5	4.2	87.9	9.1	10.4
Zn	105	4	3.4	110	10	9.1
Ga	20.1	0.5	2.5	20.0	1.2	6.0
Rb	8.38	0.77	9.1	8.70	0.40	4.6
Sr	342	11	3.0	356	8	2.2
Y	22.2	0.5	2.4	25.4	1.1	4.3
Zr	129	3	2.0	152	5	3.3
Nb	14.2	0.3	1.9	15.0	0.5	3.3
Mo	2.98	0.14	4.7	3.6	0.6	16.7
Sn	1.51	0.12	8.3	1.54	0.29	18.8
Sb	0.126	0.016	12.8	0.14	0.03	21.4
Cs	0.108	0.009	8.0	0.115	0.009	7.8
Ba	110	3	2.0	123	5	4.1
La	12.9	0.4	3.4	13.1	0.2	1.5
Ce	31.3	1.7	5.5	32.4	0.7	2.2
Pr	4.34	0.14	3.1	4.60	0.10	2.2
Nd	20.8	0.6	2.7	21.6	0.4	1.9
Sm	5.30	0.20	3.8	5.54	0.09	1.6
Eu	1.91	0.09	4.7	1.92	0.04	2.1
Gd	5.29	0.32	3.8	5.92	0.20	3.4
Tb	0.79	0.04	5.0	0.890	0.031	3.5
Dy	4.78	0.35	6.6	5.22	0.12	2.3
Ho	0.88	0.05	5.6	0.961	0.022	2.3
Er	2.26	0.10	4.3	2.54	0.07	2.8
Tm	0.30	0.01	4.5	0.331	0.001	0.3
Yb	1.95	0.12	5.9	2.10	0.05	2.4
Lu	0.26	0.01	4.6	0.285	0.009	3.2
Hf	3.53	0.16	4.6	3.93	0.14	3.6
Ta	0.88	0.05	6.2	0.961	0.022	2.3
Pb	1.94	0.06	2.9	2.07	0.10	4.8
Th	0.94	0.04	4.3	1.02	0.03	2.9
U	0.53	0.08	14.5	0.548	0.016	2.9

U: Uncertainty at 95% confidence level; % var.: percent of variability calculated.

Table 9. Mean obtained value for 12 determinations in $\text{mg}\cdot\text{kg}^{-1}$ for basalt glass ML-3BG, compared with values quoted in [15].

Elements	Obtained values			Jochum <i>et al.</i> [15]		
	Mean	sd	% rsd	Mean	U	% var.
Li	4.25	0.15	3.6	4.5	0.4	8.9
Sc	28.8	1.2	4.3	31.6	2.9	9.2
Ti	13198	836	6.3	12767	1259	9.9
V	264	6.9	2.6	268	23	10.5
Cr	154	4	2.9	179	44	24.6
Mn	1193	42	3.5	1224	108	8.9
Co	40.2	1.5	3.8	42.0	6.0	14.3
Ni	97.2	2.5	2.6	103	9	8.7
Cu	107	3	2.5	110	9	8.2
Zn	110	5	4.5	102	21	20.6
Ga	19.0	0.4	2.1	18.5	2.8	15.1
Rb	5.68	0.25	4.3	5.82	0.6	10.3
Sr	308	12	3.9	309	12	3.9
Y	21.1	1.2	5.6	23.3	1.7	7.3
Zr	105	6	5.3	117	8	6.8
Nb	7.99	0.34	4.2	8.43	0.38	4.5
Mo	15.5	0.9	5.8	16.1	3.4	21.1
Sn	1.17	0.08	6.6	1.15	0.48	41.7
Sb	0.123	0.015	12.2	0.11	0.04	36.4
Cs	0.131	0.011	8.5	0.137	0.027	19.7
Ba	74.5	2.5	3.3	79.2	4.1	5.2
La	8.84	0.30	3.4	9.04	0.45	5.0
Ce	22.5	0.8	3.4	23.2	0.9	3.9
Pr	3.23	0.15	4.5	3.42	0.14	4.1
Nd	16.2	0.5	2.8	16.9	0.6	3.6
Sm	4.58	0.18	3.9	4.74	0.24	5.1
Eu	1.62	0.09	5.7	1.67	0.06	3.6
Gd	4.65	0.35	7.4	5.10	0.32	6.3
Tb	0.72	0.03	4.9	0.783	0.057	7.3
Dy	4.45	0.39	8.8	4.84	0.21	4.3
Ho	0.85	0.05	6.2	0.901	0.051	5.7
Er	2.21	0.16	7.1	2.41	0.13	5.4
Tm	0.30	0.02	7.1	0.324	0.02	6.2
Yb	1.97	0.10	5.2	2.06	0.12	5.8
Lu	0.27	0.023	8.7	0.287	0.019	6.6
Hf	2.97	0.24	8.2	3.14	0.20	6.4
Ta	0.52	0.04	7.0	0.552	0.033	6.0
Pb	1.30	0.07	5.5	1.40	0.15	10.7
Th	0.51	0.03	5.0	0.55	0.03	5.5
U	0.41	0.020	4.9	0.448	0.055	12.3

U: Uncertainty at 95% confidence level; % var.: percent of variability calculated.

Table 10. Mean obtained values for 10 determinations in $\text{mg}\cdot\text{kg}^{-1}$ for andesite glass StHs6/80G, compared with values quoted in [15].

Elements	Obtained values			Jochum <i>et al.</i> [15]		
	Mean	sd	% rsd	Mean	U	% var.
Li	18.0	1.11	6.2	21.7	3.8	17.5
Sc	10.4	0.46	4.4	11.9	1.3	10.9
Ti	4887	103	2.1	5591	487	8.71
V	76.5	2.95	3.9	88.0	8.0	9.10
Cr	12.1	0.53	4.4	15.5	3.4	21.9
Mn	528	17	3.3	558	31	5.56
Co	10.9	0.55	5.0	13.6	1.6	11.8
Ni	15.7	0.57	3.6	23.4	7.1	30.3
Cu	29.5	1.66	5.6	42.0	13.4	31.9
Zn	60.8	4.23	7.0	71.0	10.0	14.1
Ga	18.0	0.72	4.0	22.0	5.10	23.2
Rb	24.1	0.94	3.9	31.7	4.40	13.9
Sr	462	17.2	3.6	477	21.0	4.42
Y	10.8	0.64	5.9	11.4	1.10	9.65
Zr	105	6.00	5.7	115	10.0	8.70
Nb	6.31	0.29	4.6	6.90	0.55	7.97
Mo	1.42	0.10	7.3	1.80	0.80	44.4
Sn	1.05	0.16	15.5	1.10	0.30	27.3
Sb	0.20	0.04	21.3	0.18	0.09	50.0
Cs	1.29	0.03	2.3	1.75	0.23	13.1
Ba	277	6.28	2.3	298	15.0	5.0
La	11.5	0.42	3.6	12.1	0.70	5.8
Ce	23.8	0.74	3.1	26.3	1.20	4.6
Pr	2.97	0.11	3.8	3.21	0.16	5.0
Nd	12.7	0.35	2.8	13.0	0.60	4.6
Sm	2.59	0.13	5.2	2.79	0.12	4.3
Eu	0.95	0.03	2.7	0.96	0.05	4.8
Gd	2.56	0.18	7.0	2.55	0.20	7.8
Tb	0.33	0.02	4.8	0.37	0.02	6.3
Dy	2.09	0.13	6.1	2.22	0.15	6.8
Ho	0.40	0.03	7.7	0.42	0.03	6.7
Er	1.09	0.03	3.1	1.19	0.08	6.7
Tm	0.16	0.02	10.6	0.17	0.02	8.8
Yb	1.10	0.05	4.6	1.14	0.08	7.0
Lu	0.16	0.02	9.8	0.17	0.02	10.2
Hf	2.78	0.18	6.4	2.98	0.21	7.0
Ta	0.39	0.01	3.9	0.42	0.04	8.5
Pb	10.4	0.50	4.8	10.4	1.97	18.9
Th	2.18	0.08	3.5	2.30	0.21	9.1
U	0.91	0.04	4.5	1.02	0.11	10.8

U: Uncertainty at 95% confidence level; % var.: percent of variability calculated.

Table 11. Mean obtained values for 6 determinations in $\text{mg}\cdot\text{kg}^{-1}$ for quartz diorite glass T-1G, compared with values quoted in [15].

Elements	Obtained values			Jochum <i>et al.</i> [15].		
	Mean	sd	% rsd	Mean	U	% var.
Li	19.7	0.4	2.0	20.2	1.6	7.9
Sc	30.12	0.37	1.2	27.1	2.4	8.9
Ti	5255	83	1.6	4699	210	4.5
V	167	3	2.1	190	16	8.4
Cr	15.7	0.6	3.9	20.3	1.5	7.4
Mn	942	15	1.6	968	93	9.6
Co	17.0	0.3	2.0	19.1	1.8	9.4
Ni	8.38	0.22	2.6	10.7	2.4	22.4
Cu	16.4	0.3	1.9	18.5	2.2	11.9
Zn	60.3	2.2	3.6	69	12	17.4
Ga	18.3	0.2	1.3	19.8	1.5	7.6
Rb	74.7	1.6	2.1	80.5	9	11.2
Sr	282	5	1.8	283	16	5.7
Y	28.2	0.3	1.2	24.1	1.8	7.5
Zr	169	2	1.3	141	12	8.5
Nb	8.41	0.15	1.8	8.92	0.53	5.9
Mo	5.60	0.19	3.3	3.6	2.5	69.4
Sn	1.70	0.15	8.7	1.8	0.6	33.3
Sb	0.26	0.03	10.8	0.23	0.08	34.8
Cs	2.59	0.08	3.1	2.58	0.39	15.1
Ba	385	8	2.1	393	23	5.9
La	78.0	1.6	2.0	72.1	4.7	6.5
Ce	121	2	1.9	129	6	4.7
Pr	12.8	0.2	1.7	12.5	0.8	6.4
Nd	46.3	0.8	1.8	42	2.5	6.0
Sm	7.31	0.20	2.8	6.58	0.33	5.0
Eu	1.22	0.05	4.0	1.20	0.07	5.8
Gd	8.41	0.49	5.8	5.32	0.67	12.6
Tb	0.85	0.02	2.7	0.74	0.044	5.9
Dy	5.24	0.15	2.9	4.49	0.30	6.7
Ho	1.06	0.02	2.3	0.867	0.067	7.7
Er	2.98	0.13	4.4	2.51	0.15	6.0
Tm	0.43	0.03	8.2	0.352	0.032	9.1
Yb	2.89	0.13	4.5	2.39	0.24	10.0
Lu	0.44	0.01	3.2	0.353	0.035	9.9
Hf	4.44	0.06	1.4	3.80	0.33	8.7
Ta	0.54	0.03	4.9	0.464	0.038	8.2
Pb	8.29	0.22	2.7	12	3.1	25.8
Th	36.0	0.5	1.5	31.2	2.7	8.7
U	1.44	0.04	3.0	1.72	0.26	15.1

U: Uncertainty at 95% confidence level; % var.: percent of variability calculated.

Table 12. Mean obtained values for 6 determinations in $\text{mg}\cdot\text{kg}^{-1}$ for komatiite GOR-128G, compared with values quoted in [15].

Elements	Obtained values			Jochum <i>et al.</i> [15]		
	Mean	sd	% rsd	Mean	U	% var.
Li	8.33	0.44	5.3	12.2	1.5	12.3
Sc	35.6	1.5	4.3	32.5	1.8	5.5
Ti	1865	75	4.0	1811	192	10.6
V	138	4	2.6	191	17	8.9
Cr	1868	53	2.9	2364	222	9.4
Mn	1111	14	1.2	1416	232	16.4
Co	73.2	1.1	1.4	95.7	9.8	10.2
Ni	840	32	3.8	1076	106	9.9
Cu	48.3	4.2	8.6	64.5	17.3	26.8
Zn	56.2	3.6	6.5	75.0	4.6	6.1
Ga	7.68	0.29	3.8	9.04	1.11	12.3
Rb	0.27	0.03	10.7	0.40	0.04	10.9
Sr	29.2	1.3	4.3	29.5	1.9	6.4
Y	12.5	0.3	2.4	11.8	1.2	10.2
Zr	10.5	0.4	3.8	9.8	1.1	11.2
Nb	0.091	0.005	5.9	0.096	0.012	12.5
Mo	0.43	0.06	14.2	0.73	0.27	37.0
Sn	0.35	0.05	15.4	0.23	0.10	42.7
Sb	<0.03			0.006	0.002	33.3
Cs	0.16	0.02	11.6	0.24	0.05	21.9
Ba	0.94	0.09	10.0	1.06	0.07	6.6
La	0.118	0.019	15.8	0.118	0.007	5.9
Ce	0.38	0.03	9.0	0.45	0.03	6.3
Pr	0.091	0.015	15.9	0.098	0.005	5.1
Nd	0.76	0.10	13.6	0.78	0.10	12.9
Sm	0.51	0.07	14.4	0.51	0.04	7.6
Eu	0.25	0.04	16.9	0.26	0.02	6.1
Gd	1.19	0.10	8.4	1.15	0.11	9.6
Tb	0.25	0.02	8.7	0.25	0.03	10.1
Dy	1.96	0.13	6.7	1.97	0.18	9.1
Ho	0.45	0.03	7.6	0.44	0.04	9.9
Er	1.49	0.08	5.3	1.40	0.14	10.0
Tm	0.212	0.011	5.2	0.21	0.02	8.8
Yb	1.46	0.09	6.2	1.41	0.14	9.9
Lu	0.22	0.03	14.3	0.20	0.02	10.3
Hf	0.34	0.08	24.0	0.34	0.04	10.5
Ta	0.019	0.009	45.7	0.019	0.002	10.5
Pb	0.21	0.04	16.8	0.33	0.06	19.3
Th	0.012	0.005	45.1	0.008	0.002	25.0
U	0.009	0.004	42.9	0.012	0.002	12.7

U: Uncertainty at 95% confidence level; % var.: percent of variability calculated.

Table 13. Mean obtained values for 6 determinations in $\text{mg}\cdot\text{kg}^{-1}$ for komatiite glass GOR-132G, compared with values quoted in [15].

Elements	Obtained values			Jochum <i>et al.</i> [15]		
	Mean	sd	% rsd	Mean	U	% var.
Li	8.18	0.48	5.8	9.6	1.0	10.4
Sc	38.9	2.87	7.4	37.2	1.6	4.3
Ti	2090	103	4.9	1954	144	7.4
V	185	8	4.5	219	25	11.4
Cr	2257	120	5.3	2640	207	7.8
Mn	1056	50	4.7	1138	108	9.5
Co	84.8	4.1	4.8	94.5	10.7	11.3
Ni	994	43	4.4	1187	58	4.9
Cu	169	8	4.9	208	20	9.6
Zn	54.7	2.7	4.9	79.9	16.2	20.3
Ga	9.28	0.59	6.4	10.1	1.3	12.9
Rb	1.59	0.13	8.2	2.1	0.22	10.5
Sr	14.7	0.9	6.3	15.1	1.3	8.6
Y	12.6	0.9	6.8	13.0	1.0	7.7
Zr	9.44	0.77	8.2	9.7	0.8	8.2
Nb	0.06	0.02	27.6	0.07	0.03	37.7
Mo	25.0	2.0	8.0	29.9	4.0	13.4
Sn	0.35	0.16	46.5	0.34	0.09	26.5
Sb	0.07	0.03	44.0	0.04	0.02	50.0
Cs	6.26	0.14	2.2	7.12	1.23	17.3
Ba	0.73	0.10	13.2	0.82	0.14	17.6
La	0.084	0.010	12.1	0.084	0.006	7.1
Ce	0.34	0.03	8.0	0.40	0.04	10.8
Pr	0.082	0.006	7.0	0.087	0.006	6.9
Nd	0.70	0.07	9.3	0.68	0.03	5.0
Sm	0.50	0.07	14.3	0.50	0.03	6.3
Eu	0.27	0.02	8.6	0.25	0.02	6.3
Gd	1.13	0.11	10.0	1.16	0.09	7.8
Tb	0.27	0.03	12.8	0.26	0.02	7.6
Dy	2.08	0.14	6.9	2.16	0.14	6.5
Ho	0.49	0.07	14.2	0.49	0.04	7.1
Er	1.56	0.14	9.1	1.53	0.10	6.5
Tm	0.24	0.03	11.4	0.23	0.02	7.3
Yb	1.54	0.12	7.5	1.60	0.09	5.6
Lu	0.23	0.02	10.3	0.24	0.02	8.0
Hf	0.28	0.07	24.3	0.35	0.04	10.0
Ta	0.035	0.002	5.8	0.030	0.003	10.0
Pb	17.1	0.80	4.7	19.5	2.8	14.4
Th	0.007	0.005	77.4	0.009	0.003	33.3
U	0.035	0.006	16.6	0.049	0.010	20.4

U: Uncertainty at 95% confidence level; % var.: percent of variability calculated.

Figure 2. Variation diagrams obtained for the REE contents in the BHVO-2G, BCR-2G and BIR-1G basaltic glasses, normalized with C1 chondrite [16] [17].

Figures 3-5 show the variations in obtained and preferred mean values for the Max Planck RM's (basaltic glasses KL-2G and ML-3BG, andesite StHs6/80G and quartz diorite T-1G, komatiites GOR-128 and GOR-132G). In these diagrams the observed errors are calculated for our obtained results compared with the preferred values for these materials cited in [17].

Variations diagrams for REE are presented in **Figures 6-8** normalized with respect to the C1 chondrite [16] [17].

Figure 3 shows that most of the obtained values are placed between 85% and 115% of the expected mean values; the exception is Mo in KL-2G. The values obtained for the REE in basalts ML-3BG and KL-2G (**Figure 6**) are very close to the expected ones.

Some obtained values shown in **Figure 4** are higher than the recommended figures cited for the medium to heavy REE and for Y, Zr, Mo and Ti in the quartz diorite T-1G, but lower than the recommended figures for Cr, Pb, Ni and Zn. These results may be caused by some tiny inhomogeneity of the reference material, locally concentrating heavy REE and HFSE and diluting the concentration of elements like Cr, Pb, Ni, Zn and Sn, as shown by [18] for the RM ATHO-1G.

The obtained values compared with the expected ones for the andesite glass StHs6/80G are somewhat outside the limit of $\pm 15\%$ for the following elements: Li, Cr, Co, Ni, Cu, Ga, Rb, Mo and Cs. Chromium and Ni deficiencies are also observed in T-1G, possibly indicating calibration problems, other than inhomogeneous distribution. The REE variation diagram, presented in **Figure 7**, shows that the obtained values for andesite StHs6/80G is very close to the expected values, while the medium to heavy REE in T-1G shows increased values.

In komatiite GOR-128 (**Figure 5**), the main elements showing diminished values in relation to the expected ones are Li, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Mo, Cs, Pb, U. In sample GOR-132G (**Figure 5**) the same relationship is observed for elements Ni, Cu, Zn, Rb, Mo, Cs, Ce, Th and U. These elements show values that are very much increased or diminished when compared with NIST-612, which may not be the best calibration material to be used for this exercise. On the other hand, lack of homogeneity (see [19] and [20]) may be another explanation, possibly caused by quench crystallization of olivine, which could sequester some elements. A larger set of analytical data, not restricted to our limited number of determinations, is needed. The REE variation diagrams presented in **Figure 8** (komatiites) show that the obtained values are close to the certified values.

5. Conclusions

The obtained values for the several reference materials made available by the USGS and the Max Planck Institute cover a rather wide spectrum of elemental abundances for the over 40 elements determined with the LA-Q-ICPMS technique, the methodology used in this contribution.

Figure 3. Average values obtained in relation to preferred values for several elements in basalt glasses KL-2G and ML-3BG, compared with the mean values cited in [17], cf. Table 8 and Table 9.

Figure 4. Average values obtained in relation to preferred values for several elements in glasses T-1G (quartz diorite) and StHs6/80G (andesite), compared with the mean certified values cited in [17], cf. Table 10 and Table 11.

The used technique provides high quality results, in terms of analytical accuracy, and is also very fast. The samples can be prepared as thin sections, with a thickness of around 40 to 60 microns, or as mineral grains mounted within polished epoxy resins.

Interferences can be kept at minimum levels, a result achieved with the use of dry plasma, thereby diminishing the influence of agents such as present in aqueous acid systems (O^{2-} , OH^- , Cl^- , NO_3^- , etc.). However, isotopes such as ^{135}Ba , ^{139}La , ^{140}Ce , and others may interfere on medium and heavy REE, even if the level of oxides is kept below the recommended value of 1%. Increased values of some REE may be caused by the generation of several spurious REE molecular species (e.g. [21]). The point is illustrated in Figure 6, where ^{155}Gd may owe its increase to interference by $^{139}La^{16}O^+$. Careful selection of isotope species is therefore recommended, before relying on one or the other isotopes for analytical calibrations.

Figure 5. Average values obtained in relation to preferred values for several elements in komatiite glasses GOR-128 and GOR-132G, compared with the mean certified values cited in [17], cf. Table 12 and Table 13.

Figure 6. Variation diagrams obtained for the REE contents in basaltic glasses KL-2G and ML-3BG, from the Max Planck Institute, normalized with the C1 chondrite [16] [17].

The rock glasses prepared by the Max Planck Institute cover an adequate spectrum of elements important for studies in igneous petrology, but the materials seem to present a lack of homogeneity for some elements, depending on the analyzed mass and of the spot used for identification [15] and may therefore be the cause for the observed discrepancies in obtained results. More tests are certainly needed to test statistically this hypothesis, in order to certify these glasses as proper equivalents of the USGS materials.

The use of internal standards, especially MgO and CaO, is a necessary tool to standardize obtained results with our discussed technique. But many minerals may lack sufficient contents of CaO to be subjected to the LA-Q-ICPMS methodology, a fact that limits the scope of the glasses prepared by NIST, with low to very low MgO contents [22] [23]. Another factor to be considered is the possibility of fractionation of many elements, depending on the used internal standard [24]. There is certainly a need to continue the search for an adequate preparation of proper rock standards to be used for LA studies in minerals.

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Figure 7. Variation diagrams obtained for the REE contents in basaltic glasses StHs6/80G (andesite) and T-1G (quartz diorite), from the Max Planck Institute, normalized with the C1 chondrite [16] [17].

Figure 8. Variation diagrams obtained for the REE contents for komatiite glasses GOR-128 and GOR-132G, from the Max Planck Institute, normalized with the C1 chondrite [16] [17].

tion of the spectrometer Q-ICPMS (1999/04824-9) and Laser Ablation System (2004/08856-2) and maintenance and update of the Laboratório de Química e ICP-OES/MS of the Instituto de Geociências, University of São Paulo. This is a contribution of the newly created Geoanalítica-USP Core Facility at the same institute, devoted to mineralogical and petrological studies. Support was also provided by a grant from FAPESP (Nr. 2012/06082-6, coordinator, Prof. Excelso Ruberti).

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ANEXO C

Manuscript Number:

Title: Timing and sources of granite magmatism in the Ribeira Belt, SE Brazil: insights from zircon in situ U-Pb dating and Hf isotope geochemistry in granites from the São Roque Domain

Article Type: SI: Granite magmatism

Keywords: Ribeira Belt
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Abstract: Eight new in situ U-Pb zircon age determinations by Shrimp and LA-MC-ICPMS reveal that the main granite magmatism in the São Roque Domain, which is largely dominated by high-K calc-alkaline monzogranites with subordinate peraluminous leucogranites, occurred between 604 ± 3 and 591 ± 4 Ma. Importantly, this small temporal range is ca. 20-30 Ma younger than previously admitted based on U-Pb TIMS dates from literature, some of which obtained in the same occurrences now dated. The observed discrepancy seems related to the presence of small Paleoproterozoic inherited cores in part of the zircon populations used for TIMS dating, which could also respond for the unusually high (up to 10 Ma) uncertainty associated with most of these ages. The younger age range now identified for the São Roque granite magmatism has important implications for the evolution of the Ribeira Fold Belt. Whilst previously admitted ages ca. 620-630 Ma substantiated correlations with the widespread and intensely foliated high-K calc-alkaline granitoid rocks of the neighbor Socorro-Guaxupé Thrust Nappe (potentially associated with an accretionary continental margin), the ~ 600-590 Ma interval seems more consistent with a late deformation tectonic setting.

Strongly negative $\epsilon_{\text{Hf}}(t)$ characterize the magmatic zircons from the São Roque Domain granites. An eastward increase from -22 in the São Roque Granite to -11 in the Cantareira Granite and neighboring stocks suggests an across-domain shift in granite sources. Such eastward younging of sources, also indicated by Sm-Nd isotope data from granites and supracrustal sequences in neighboring domains, is suggestive that some of the first-order limits and discontinuities in this belt are not defined by the strike-slip fault systems traditionally taken to separate distinct domains. Although the negative $\epsilon_{\text{Hf}}(t)$ and $\epsilon_{\text{Nd}}(t)$ indicate sources with long crustal residence for all studied granite plutons, the observed range is more radiogenic than the values calculated at 600 Ma for both the Mesoproterozoic (1.5-1.8 Ga) passive-margin metavolcano-sedimentary sequences of the São Roque Domain and their inferred Archean to Paleoproterozoic continental sources. Therefore, a contribution from sources with less negative $\epsilon_{\text{Hf}}(t)$ and $\epsilon_{\text{Nd}}(t)$ is required to explain the observed range.

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COVER LETTER

This manuscript is directed to the Special Issue “Granite magmatism in Brazil”, connected with the 8th Hutton Symposium, Florianópolis, 20-25 of September, 2015.

It presents new in situ U-Pb zircon age determinations by Shrimp and LA-ICPMS for typical granites from the São Roque Domain (Ribeira Belt, SE Brazil) and reveals ages in a short time range (603-590 Ma) that is ~20-30 Ma younger than expected from previous TIMS dating. The previous dates are interpreted as unreliable, probably due to inclusion of small proportions of inherited cores, evidenced by CL imaging. The new ages are considered within the tectonic framework of granite magmatism in the Ribeira Belt, and appear consistent with a post-collisional environment.

In situ Hf isotope ratios were obtained in the same zircon crystals dated, and are used in conjunction with whole-rock Nd isotope ratios to infer sources of the granite melts. Comparison with the ~600 Ma Hf and Nd signatures of potential sources require that a younger component with less negative $\epsilon_{\text{Hf}}(t)$ and $\epsilon_{\text{Nd}}(t)$ contributes to granite melts; in most cases, it may correspond to a mantle input. An eastward younging of the crustal sources is suggested by combined Nd-Hf data. Older Archean crust is an important component in the westernmost occurrence (São Roque Granite) whereas Paleoproterozoic crust (juvenile at ~2.4-2.5 Ga; reworked at 2.1-2.2 Ga) is the most important source of most occurrences, including the Itaquí and Cantareira granites and the Perus tourmaline granite. A contribution from younger crust (~2.1 Ga juvenile Ga crust?) revealed by Hf signature of inherited zircons from the Tico-Tico Granite is identified in some of the easternmost occurrences.

Timing and sources of granite magmatism in the Ribeira Belt, SE Brazil: insights from zircon in situ U-Pb dating and Hf isotope geochemistry in granites from the São Roque Domain

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Abstract

Eight new in situ U-Pb zircon age determinations by Shrimp and LA-MC-ICPMS reveal that the main granite magmatism in the São Roque Domain, which is largely dominated by high-K calc-alkaline monzogranites with subordinate peraluminous leucogranites, occurred between 604±3 and 591±4 Ma. Importantly, this small temporal range is ca. 20-30 Ma younger than previously admitted based on U-Pb TIMS dates from literature, some of which obtained in the same occurrences now dated. The observed discrepancy seems related to the presence of small Paleoproterozoic inherited cores in part of the zircon populations used for TIMS dating, which could also respond for the unusually high (up to 10 Ma) uncertainty associated with most of these ages. The younger age range now identified for the São Roque granite magmatism has important implications for the evolution of the Ribeira Fold Belt. Whilst previously admitted ages ca. 620-630 Ma substantiated correlations with the widespread and intensely foliated high-K calc-alkaline granitoid rocks of the neighbor Socorro-Guaxupé Thrust Nappe (potentially associated with an accretionary continental margin), the ~ 600-590 Ma interval seems more consistent with a late deformation tectonic setting. Strongly negative εHf(t) characterize the magmatic zircons from the São Roque Domain granites. An eastward increase from -22 in the São Roque Granite to -11 in the Cantareira Granite and neighboring stocks suggests an across-domain shift in granite sources. Such eastward younging of sources, also indicated by Sm-Nd isotope data from granites and supracrustal sequences in neighboring domains, is suggestive that some of the first-order limits and discontinuities in this belt are not defined by the strike-slip fault systems traditionally taken to separate distinct domains. Although the negative εHf(t) and εNd(t) indicate sources with long crustal residence for all studied granite plutons, the observed range is more radiogenic than the values calculated at 600 Ma for both the Mesoproterozoic (1.5-1.8 Ga) passive-margin metavolcano-sedimentary sequences of the São Roque Domain and their inferred Archean to Paleoproterozoic

continental sources. Therefore, a contribution from sources with less negative $\epsilon_{\text{Hf}}(t)$ and $\epsilon_{\text{Nd}}(t)$ is required to explain the observed range.

1. Introduction

The use of *in situ* techniques (Shrimp and LA-ICPMS) for U-Pb zircon dating offers, besides the obvious advantages of simplified preparation procedures and speed of analysis, the opportunity of avoiding crystal domains with evidence of inheritance or late disturbance as an important bonus. Even though the achieved precision of both techniques (typically 1% relative, or ± 5 Ma at ~ 600 Ma) does not permit to resolve temporally events identified by field criteria in many individual plutonic bodies, in some cases they may be advantageous over the more precise TIMS technique. In particular, they allow obtain a large number of concordant ages in texturally-controlled portions of the crystals that are fundamental to unambiguously identify true magmatic crystallization ages. This is particularly true when determining the crystallization ages of granitic rocks from some parts of the Ribeira Belt in SE Brazil, where previous TIMS U-Pb zircon dating has revealed the frequent presence of inheritance (e.g., Janasi et al., 2001; Prazeres Filho et al., 2003). In fact, the influence of inheritance may be too difficult to avoid when multi-grain fractions or even single grains are used, which may in practice result in imprecise and sometimes unreliable ages.

The São Roque Domain is a fault-bounded segment of the Ribeira Belt that corresponds to the northern extension of the Apiaí Terrane, mostly composed of ~ 1.8 - 1.4 Ga meta-volcanosedimentary sequences of rift and passive-margin character, which were metamorphosed and intruded by large volumes of granite in the late Neoproterozoic (Ediacaran). In this study, we selected seven among the most representative granite plutons from the São Roque Domain to perform U-Pb zircon dating by Shrimp and LA-ICPMS; some of them were previously dated by TIMS, but the results remained unpublished and carry relatively high (8-12 Ma) uncertainties (Topfner, 1996; Ragatky, 1998).

We also determined Hf isotope ratios in the same portions of crystals sampled for U-Pb dating, thus pioneering the use of this isotope system for granites in this domain. The Hf isotope system revealed a particularly useful tool for inferences on the petrogenesis and tectonic significance of the São Roque granites, especially when integrated with previous geological and geochemical studies, including whole-rock Sm-

Nd isotope data, which were complemented by some new determinations presented here.

2. Geological setting

2.1. *The São Roque Domain in the tectonic framework of SE Brazil*

The Ribeira Belt corresponds to the central segment of an extensive Neoproterozoic orogenic system running roughly parallel to the present Atlantic coastline from latitude 16°S in Brazil to 35°S in Uruguay. The northern ~N-S oriented segment of this system from latitude 16° to 21° S is the Araçuaí Belt (Fig. 1) where, after a series of Mesoproterozoic rifting episodes, a passive margin developed at the eastern margin of a continental mass stabilized at ~2.05 Ga (the São Francisco craton). After ca. 800 Ma, this evolved to an active margin with the closure of an ocean that lied between the São Francisco and Congo cratons (Alkmim et al., 2006).

The continuity of a stable cratonic area west of the Ribeira and (south of latitude 27°S) Dom Feliciano belts is less obvious, mostly due to cover by the extensive Phanerozoic Paraná Sedimentary Basin (Fig. 1). Geophysical evidence has been used to infer the presence of cratonic blocks beneath the Paraná Basin (the hidden Paranapanema “craton” of Mantovani & Brito Neves, 2005, and the northern continuation of the Rio de la Plata craton; Rapela et al., 2007). In many current tectonic models, these “cratonic blocks” would have amalgamated to each other and to the São Francisco Craton in earlier episodes of Neoproterozoic evolution, before accretion of the eastern terrains of the Ribeira and Dom Feliciano belts.

The metavolcano-sedimentary sequences comprising the Ribeira Belt correspond to passive margin deposits developed mostly from 1.8 to 1.4 Ga in the Apiaí Terrane (Siga Jr. et al., 2011, Juliani et al., 2000), and possibly later in the eastern Embu Terrane. Expressive magmatic arc terranes are recognized east of both the Ribeira Belt (the Rio Negro arc; Tupinambá et al., 2012) and the Dom Feliciano Belt (the Florianópolis-Pelotas batholith and African counterparts, Basei et al., 2005). Magmatic arc activity and related plate convergence are inferred to have started as early as 800 Ma, and no discontinuity with arc systems associated with the Araçuaí Belt is described. Moreover, evidence of expressive granite generation beginning at ca. 780 Ma is

widespread in the easternmost portion of the Ribeira Belt (Embu Terrane; Vlach, 2001; Cordani et al. 2002).

The São Roque Domain (SRD) is one of several fault-bounded blocks that make up the south Ribeira Belt, and represents the northeastern portion of the Apiaí Terrane (Fig. 1; Campos Neto 2000; Heilbron et al., 2008). Our recent work on sedimentary provenance in metasediments from the SRD (Henrique-Pinto et al., 2014) indicates source areas that are very similar to the São Francisco craton, leading to the suggestion that the Apiaí Terrane corresponds to the SW extension of the eastern passive margin of the São Francisco Paleoplate, an interpretation that is consistent with gravity data (Rocha 2009).

The SRD hosts meta-volcano-sedimentary sequences of dominantly Mesoproterozoic ages (e.g., Hackspacher et al., 2000; Juliani et al., 2000; Henrique-Pinto and Janasi, 2010) and is, like all other domains of the Ribeira Belt, intruded by significant volumes of Neoproterozoic granites. The SRD is bordered to the north by the Socorro-Guaxupé Nappe (SGN), an allochthonous high-grade terrane that exposes a large (~20 km) vertical section of the Neoproterozoic crust also intruded by large volumes of granites and whose origin is alternatively linked in the literature to the Brasília or to the Ribeira Belt.

2.2. *Neoproterozoic granite magmatism in the São Roque Domain*

Neoproterozoic granite magmatism is widespread and voluminous in the Ribeira Belt and has been subject of several reviews in recent years (e.g., Janasi & Ulbrich, 1991; Heilbron et al., 2004). Most of the granites were generated in a <100 Ma time interval (650-560 Ma), but significantly older and younger manifestations are reported (e.g., ~750-800 Ma occurrences of orthogneiss from several domains, and the ~500 Ma “G5” granites found only in the Costeiro Domain), expanding the whole history of Neoproterozoic granitic magmatism to a range of as much as 300 Ma. It is well known, on the other hand, that the age range of peak magmatism may be shorter within individual domains, and shows a regional shift, with a general tendency to be younger toward SE; this pattern is followed by the ages of the post-orogenic magmatism, indicating progressive stabilization of the fold belt in this direction.

Granites from the SRD occur as a series of plutons whose shapes are often strongly controlled by NE-directed transcurrent faults (Fig. 2), indicating that their emplacement overlapped the development of the Ribeira Belt strike-slip tectonics. By far the most typical granite type forming the largest plutons is a porphyritic biotite monzogranite to granodiorite/quartz monzonite with K-feldspar megacrysts (2-4 cm in length) set in a medium to coarse-grained matrix. The metaluminous character of these granites is indicated by the presence of abundant accessory titanite; hornblende is present in the more mafic samples, but may be rare in some occurrences. Chemically, they are usually SiO₂-poor, often straddling the limit between acid and intermediate rocks (64-68% SiO₂); relatively high mg# (35-45) and high K/Na are typical, thus classifying as high-K calc-alkaline (HKCA) granites (Fig. 4). Other typical geochemical signatures are fractionated REE patterns lacking significant negative Eu anomalies, high contents of LILE (Ba= 1000-2000 ppm; Sr= 600-1000 ppm), and high Sr/Y (often >30).

A contribution from contemporaneous mafic magmatism is evident in some occurrences, in the form of scattered mafic synplutonic dykes and mafic microgranular enclaves. Often more evident are evidences of contamination by assimilation of metasedimentary rocks, which may appear as xenoliths or strongly modified mica-rich enclaves.

Two elongated plutons with subalkaline affinities occur at the westernmost portion of the SRD, both showing locally the rapakivi texture, and considered in some works as of post-orogenic character. The São Francisco Granite fits better into the definition of A-type granites, as it is dominated by fractionated, high-SiO₂ granites, with low Sr (<100 ppm) and weakly fractionated REE patterns ((La/Yb)_N= 12-15 with strongly negative Eu anomalies (Eu/Eu* = 0.2-0.3) (Wernick et al., 1993; Godoy et al., 2010). The Sorocaba Granite, with characteristic elongated shape, is constituted of usually non-deformed more mafic porphyritic monzogranites; although chemically distinct from the HKCA granites (e.g., < 300 ppm Sr, moderately fractionated ((La/Yb)_N= 15-20) REE patterns with negative Eu anomalies (Eu/Eu* = 0.4-0.6)) is of more ambiguous affinity.

Other minor occurrences of subalkaline granite are known from the central portion of the SRD, as late occurrences within the Cantareira Granite (the Canivete type of Dantas, 1990) and the deformed Vila dos Remédios Quartz Syenite.

The Tico-Tico Granite is a small E-W elongated (7 x 1.5 km; area= 10 km²) occurrence, but constitutes the largest pluton entirely composed of frankly peraluminous

1 biotite-muscovite leucogranite in the SRD. Smaller occurrences may occur within the
2 largest HKCA plutons (especially in the São Roque Granite, Fig. 3a) or as isolated
3 bodies, among which the peculiar garnet-tourmaline aplite-pegmatite Perus Granite is
4 the most outstanding.
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7 A large number of medium-sized granite plutons of diverse composition occur at
8 the easternmost portion of the SRD (Igaratá region). These were grouped by Campos
9 Neto et al. (1983) in several suites, on the basis of variations in modal composition
10 (monzogranite to granodiorite/quartz monzonite, with small diorite bodies), mineralogy
11 (usually metaluminous to marginally peraluminous) and texture (porphyritic to
12 equigranular; foliated to massive). Geochemical and Sr-Nd isotope data for these
13 granites were presented by Ragatky (1998), and revealed predominance of high-K calc-
14 alkaline granites that, although in some cases are similar to the main plutons from the
15 central SRD, are commonly less Ba and Sr-rich and show more radiogenic Nd isotope
16 signatures (see below).
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29 **3. Methods**

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32 In situ isotope determinations in zircon by LA-MC-ICPMS and Shrimp aiming
33 to obtain space-resolved ages and Hf isotope ratios were the main tools used in this
34 work. The zircon crystals were extracted from 6-8 kg granite samples using standard
35 techniques of milling, magnetic and dense liquids concentration. Previously to the
36 microanalyses, cathodo-luminescence images were obtained from the epoxy mounts
37 with 50-100 crystals, and carefully studied to identify textural features of the zircon
38 crystals. Whole-rock major and trace-element data (by XRF and solution-ICPMS,
39 respectively) and Sr-Nd isotope data were obtained for samples chosen for our study, as
40 part of their characterization, and to allow comparison with literature data. All analyses
41 were performed in laboratories of the Instituto de Geociências, Universidade de São
42 Paulo, Brazil. Details of the analytical protocols of all methods employed are presented
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56 **4. Whole-rock and Sr-Nd isotope geochemistry**

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1 A large dataset of whole-rock geochemical analyses is available in the literature
2 for the main granite occurrences of the SRD, mostly from unpublished academic theses
3 and papers published in the local literature in the 1990's (e.g., Dantas, 1990; Andrade et
4 al., 1994; Morteani et al., 2008; Wernick et al., 1993). These data were generated in
5 different laboratories, what in some cases may respond for slight systematic differences;
6 these however do not hinder the general comparisons made here. Since the purpose of
7 this work is not explore the geochemical evolution of these occurrences, we just
8 illustrate some key features of the SRD granites in variation diagrams presented in
9 Figure 4; these diagrams are useful to set the samples studied here into the geochemical
10 variation identified in the different plutons, what will be explored in the next session.
11 Further considerations about the implications of some key geochemical aspects of the
12 SRD granites are discussed in item 6.2.1.

13 Whole-rock Sr isotope determinations are available in literature for a few
14 granites from the SRD (Tassinari, 1988; Ragatky, 1998). There is a wide variation in
15 $^{87}\text{Rb}/^{86}\text{Sr}$ ratios, reflecting changes in rock composition, from 0.2-0.5 in typical Sr-rich
16 (>700 ppm) HKCA granites through intermediate values in granites from the eastern
17 SRD (mostly 0.6-1.6; Sr= 300-700 ppm) to very high (5.5-7.7) in the peraluminous
18 Tico-Tico leucogranite.

19 The $^{87}\text{Sr}/^{86}\text{Sr}_{600}$ of high-Sr HKCA granites are within a small range (Cantareira,
20 0.710-0.711; Mairiporã, 0.7084-0.7086), which is the same of the medium-Sr granites
21 from the eastern portion of the SRD (Morro Azul, 0.709-0.712; Igaratá, 0.708-0.710),
22 where the lowest $^{87}\text{Sr}/^{86}\text{Sr}_{600}$ so far recorded in the SRD is shown by a diorite from the
23 small Boa Vista Granite (0.7063). The Tico-Tico peraluminous leucogranite has much
24 higher $^{87}\text{Sr}/^{86}\text{Sr}_{600}$ (0.717-0.725).

25 We performed Sr isotope determinations on some samples of HKCA granites
26 studied here, to place them in the regional picture and to have specific information for
27 some occurrences so far lacking this sort of data, such as São Roque, Itaquí and Taipas.
28 The $^{87}\text{Sr}/^{86}\text{Sr}_{600}$ are within a short range (0.709-0.710), overlapping results for similar
29 SRD granites; an exception is São Roque granite sample SR-07, with higher $^{87}\text{Sr}/^{86}\text{Sr}_{600}$
30 (0.712; Table 1).

31 Single-stage Sr T_{DM} ages are rarely given much significance, in view of ease of
32 Rb and Sr fractionation during magma generation in the crust. However, it is worth
33 registering that typical values for high-Sr HKCA granites are >2.0 Ga while those for
34 intermediate Sr granites from eastern SRD concentrate in the 1.0-1.4 Ga range whereas
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1 peraluminous, high Rb/Sr leucogranites such as Tico-Tico have the youngest ages
2 (0.74-0.83 Ga) (Fig. 6; see Tassinari, 1988).

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4 Only a few granites from the São Roque Domain were subject of previous
5 systematic Sm-Nd determinations, which is particularly true of the plutons from the
6 central portion of the domain studied here. However, a collection of Sm-Nd data exists
7 for plutons occurring at the westernmost (Sorocaba and São Francisco granites) and
8 easternmost (several small plutons in the Igaratá region) portions of the SRD (Dantas et
9 al., 2000 and Ragatky, 1998).

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11 The results for six new Nd isotope determinations are presented in Table 1.
12 ϵNd_{600} are negative and within the range previously known for the SRD (-15 to -9), with
13 an eastward increase in ϵNd_{600} and correspondent decrease in Nd T_{DM} (e.g., Nd T_{DM} =
14 2.15 Ga in the São Roque Granite and 1.65 in Cantareira MD-42b).

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16 ϵNd_{600} for all granite occurrences, including data from literature, are indicated in
17 Figs. 2 and 3.

28 29 **5. Zircon age and Hf isotope determinations**

30 31 *5.1. São Roque Granite*

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33 The westernmost studied pluton is the ~160 km² São Roque Granite, which has,
34 in plan, the rough shape of a triangle, with the base partly defined by the N70E-directed
35 Taxaquara Fault (Fig. 2).

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37 The pluton was mapped in detail by Andrade et al. (1994) who recognized a
38 main unit of porphyritic hornblende-biotite monzogranite to granodiorite distributed
39 throughout the pluton (Fig. 3a). This unit is intruded by small occurrences of pink to
40 gray inequigranular biotite monzogranite whose distribution suggests a discontinuous
41 body of roughly half-ring shape at the pluton's central/southeastern portion and by pink
42 medium-grained equigranular monzogranite with associated coarse-grained tourmaline-
43 muscovite granite at the pluton's northern portion (Fig. 3a).

44 45 *Sample petrography and geochemistry*

Sample SR-07 corresponds to the predominant porphyritic hornblende-biotite monzogranite typical of the São Roque Granite, and was collected in a roadcut in the Livio Tagliassachi Road (SP-053/280) close to the access to the Castelo Branco Highway (UTM coordinates of all samples used in this study are listed in Tables 2-4; full results of whole-rock geochemical analyses are in Supplementary File 2). A chemical analysis shows that the granite is relatively primitive with 64% SiO₂, 1.7% MgO, 3.2% CaO, with high K₂O (4.8%) and high K₂O/Na₂O (1.6) typical of a metaluminous high-K calc-alkaline granitic rock. A moderately fractionated chondrite-normalized REE pattern ((La/Yb)_N = 29) with a weak negative Eu anomaly (Eu*/Eu = 0.8) (Fig. 5) and high Sr/Y (40) are typical.

Sample SR-05 is an inequigranular biotite granite collected in a roadcut 7 km to the south of SR-07 along the same road. This granite has a much more evolved composition with 75% SiO₂, 0.2% MgO and 1.2% CaO, and shows a less fractionated REE pattern ((La/Yb)_N = 12) with lower LREE contents and well-defined negative Eu anomaly (Eu*/Eu = 0.57); Sr/Y is lower (19). These features suggest that, if related to the predominant São Roque granites, the magma that generated SR-05 resulted from fractionation involving plagioclase and a LREE-bearing accessory mineral.

Zircon morphology and U-Pb dating

Zircon crystals from SR-07 are short (100-200 μm), with ~2:1 aspect ratio and well developed oscillatory zoning. U contents are 600-1000 ppm (average 791 ppm), Th 350-900 ppm (average 609 ppm), and Th/U varies from 0.6 to 1.0 (average 0.76). An exception is core 23.1, with extremely high Th (9000 ppm) U (4000 ppm), Th/U 2.5, black in CL. Inherited core 18.1 (see below) has extremely low Th/U 0.02 due to Th ~3 ppm.

LA-ICPMS determinations were performed in 26 spots, and most are nearly concordant (Table 2). With the exclusion of two inherited cores and two points with larger errors, a concordia age is obtained from all remaining spots, and yields **602.6±3.8** Ma (2σ; MSWD = 0.05, probability of concordance = 0.83; Fig. 7) as the best estimate of the age of this granite.

Zircon Hf isotope geochemistry

1 The Hf isotope composition of zircons from sample SR-07 is remarkably
2 homogeneous (Fig. 9), with strongly negative $\epsilon_{\text{Hf}}(t) = -21$ to -24 (therefore spreading
3 only 3 ϵ_{Hf} , within error or individual uncertainties, which are typically 1.5 ϵ_{Hf} ; average
4 $\epsilon_{\text{Hf}}(t)$ is -22.8 ± 1.2). Inherited core 18.1 has strongly negative $\epsilon_{\text{Hf}}(t)$ (-13.5) at its
5 crystallization age (2.1 Ga), indicating derivation from reworked crust.
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10 5.2. *Itaqui Granite and Fazenda Itahyê Stock*

11 The **Itaqui Granite** is a 120 km² pluton elongated in the E-W direction,
12 extending over 24 km parallel to Taxaquara Fault, which defines its southern contact.
13 Wernick & Ferreira (1993), based on detailed mapping, recognized that the bulk of the
14 pluton was built in two main phases of intrusion.
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22 The *early phase* consists of two units of hornblende-bearing porphyritic granitic
23 rocks with 2.5-3 cm K-feldspar megacrysts. The less voluminous and more
24 differentiated monzogranite unit (with CI~6; 68-69% SiO₂; 0.8-0.9% MgO) occurs as a
25 <2 km-wide border wrapping the more primitive granodiorite unit (with CI~15; 64-65%
26 SiO₂, 1.8-2.2% MgO) along the western half of the pluton where it attains its greater
27 width (up to 8 km) (Fig. 3b).
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33 The *late phase* comprises two ellipsoidal stocks that intrude the previous units at
34 the southern portion of the pluton, and thus make up its southern contact over most of
35 its extension (Fig. 3b). Both are composed of inequigranular biotite monzogranites with
36 rare to absent K-feldspar megacrysts. The western stock (~10 x 4 km) is composed of
37 more primitive monzogranites (CI~9; 66-69% SiO₂; 0.9-1.2% MgO) as compared to the
38 eastern stock (~5 x 2 km) (CI7; 69-70% SiO₂; 0.5-0.8% MgO).
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44 Both early and late phase Itaqui granites are characteristically high-K calc-
45 alkaline (metaluminous, with 3.7-4.4% K₂O and K₂O/Na₂O = 1.3-1.0), with high Sr
46 (600-900 ppm) and Ba (1000-1900 ppm). Chondrite-normalized REE patterns are
47 typically fractionated with negligible Eu anomalies, typically with (La/Yb)_N = 50-60 in
48 the compositionally intermediate Pedreira Cantareira and Aldeia da Serra units and 30-
49 40 in the more primitive Barueri and Mutinga units (Wernick et al., 1993). Along with
50 high Sr/Y (50-60, reaching higher and extreme values in the more fractionated units,
51 ~80 in Pedreira Cantareira and 160-220 in Mutinga), this is indicative of deep-seated
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1 evolution processes not involving plagioclase fractionation, and possibly involving
2 residual garnet.

3 The **Fazenda Itahyê** granitic stock is a small ($< 2 \text{ km}^2$) granite occurrence
4 located ~3,5 km to the NE of Itaquí, and is composed of non-foliated porphyritic
5 hornblende-biotite granodiorite in all mineralogical and geochemical aspects similar to
6 more primitive unit of the Itaquí Granite early phase (cf. Supplementary File 2).
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10 *Sample petrography and geochemistry*

11 Samples ITQ-2 and ITQ-E from the Itaquí Granite were collected in the Polimix
12 quarry located at the central portion of the pluton (Fig. 3b). Apart from its lower K_2O
13 (2.9%) and Ba (620 ppm), sample ITQ-2 is a typical porphyritic biotite monzogranite
14 from the more primitive early phase unit. Sample ITQ-E is a medium- to fine-grained
15 basic enclave with 50% SiO_2 from the same quarry. Both samples have relatively high
16 mg# (0.43-0.46), Sr (~800 ppm), and fractionated REE patterns ($(\text{La/Yb})_N=31$ in ITQ-2
17 and 18 in the enclave, which has higher HREE contents) with nearly absent Eu
18 anomalies ($\text{Eu}/\text{Eu}^*=0.89$ and 0.97 , respectively).
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29 Sample MD-24 from the Fazenda Itahyê granite is a porphyritic hornblende-
30 biotite monzogranite; its chemical composition both in terms of major and trace-
31 elements is nearly identical to that of ITQ-2, apart from higher and more typical K_2O
32 (4.3%) and Ba (1350 ppm) contents.
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38 *Zircon morphology and U-Pb dating*

39 ITQ-2 crystals are 100-300 μm in length, with aspect ratio 2:1 to 4:1. Cores may
40 be unzoned or show oscillatory zoning; a few cores have convolute aspect; borders are
41 typically oscillatory zoned. Typical Th/U ratios are in the range 0.4-0.6 (average 0.44;
42 one exception with 1.1); average U is 537 ppm.
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47 Sixteen points were analyzed, by Shrimp and show small discordance (Table 3).
48 A concordia age of **595.1 $\pm$ 4.6 Ma** (MSWD= 2.1; Fig. 8) was obtained from 12 points (4
49 were discarded because of high ^{204}Pb), and is interpreted as the crystallization age of
50 this sample.
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54 ITQ-E crystals are all short, 2:1, but show two populations with equivalent
55 abundance: (1) crystals with oscillatory zoning, which may have light limpid cores in
56 CL images; (2) nearly homogeneously black crystals in CL images, which may reflect
57 high U cores; thin light rims are present in a few of these crystals.
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1 Zircon crystals from the Fazenda Itahyê sample MD-24 are short to slightly
2 elongated, with typical aspect ratios 2:1, rarely up to 4:1, and oscillator zoning. Rarely
3 do they show homogeneous cores that are CL-bright. Th/U ratios are higher than those
4 of ITQ-2 (average 0.8, varying from 0.5 to 1.1), reflecting lower U (200-500 ppm,
5 average 416 ppm); Th contents are 120-500 ppm, with average 333 ppm.
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8 A Concordia age of **598.3±3.5 Ma** (MSWD= 0.28, Fig. 7) was obtained from the
9 regression of LA-ICMS analyses of 24 spots from sample MD-24, and is considered the
10 best estimate of its magmatic crystallization age. An inherited core with the oldest age
11 obtained in this study (spot 10.1; $^{207}\text{Pb}/^{206}\text{Pb}$ age 3.3 Ga, 8% discordant) is black in CL
12 images, and has very low Th (47 ppm), and correspondingly low Th/U (0.2).
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19 ***Zircon Hf isotope geochemistry***

20 The Hf isotope composition of zircons from sample ITQ-2 is relatively
21 homogeneous, $\epsilon\text{Hf}(t)$ varying from -19.3 to -15.5 (average -17.4 ± 1.4 , 1σ ; spread of 4
22 ϵHf units; Fig. 9).
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27 Zircons from mafic enclave ITQ-E have a wide variation of $\epsilon\text{Hf}(t)$ (11 ϵHf
28 spread). Crystals from population (2), black in CL images, have markedly least negative
29 $\epsilon\text{Hf}(t)$ (-11 and -12), whereas the more negative values (-19.3 to -20.3) are associated
30 with light limpid cores in zircons from population (1) (Fig. 9). Values of $\epsilon\text{Hf}(t)$ in
31 oscillatory zoned portions are in the same range of zircons from host granite (-17.4 to -
32 14.5).
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39 The Hf isotope composition zircons from the Fazenda Itahyê granite MD-24 is
40 as homogeneous as those from Itaqui sample ITQ-2 (a 4 ϵHf units range) and has
41 similar $\epsilon\text{Hf}(t)$ (-19 to -14.5; average -16.9 ± 1.4).
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46 **5.3. Cantareira Granite and satellites**

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48 The **Cantareira Granite** is the largest granite occurrence in the São Roque
49 Domain, attaining batholithic dimensions ($\sim 360 \text{ km}^2$); an indentation of country rock
50 along its western-central portion indicates that the batholith shall correspond in reality
51 to the junction of two plutons (Fig. 3c).
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57 The *northern pluton* has an ellipsoidal shape with its main length (25 km) along
58 N45E, being wider in the SW portion (12 km); it delimited to the east by the N40E-
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1 directed Mandaqui Fault (Fig. 3c). The main rock type is a porphyritic biotite
2 monzogranite with scarce hornblende similar to the predominant granites in the São
3 Roque and Itaquí plutons. Except at its southern border, where it is intruded by the late
4 stock of more fractionated porphyritic monzogranite (Canivete facies), the border of the
5 northern pluton is made up of a variety of granite types, including banded, foliated and
6 an inequigranular more felsic variety.
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10 The *southern pluton*, like the São Roque and Itaquí granites, has its southern
11 limit defined by the Taxaquara Fault, along which it extends for ca. 12 km; it has a
12 roughly circular shape in plan, being connected to the northern pluton by a bulge that
13 has a width of 2-4 km (Fig. 3c). It is mostly constituted of a porphyritic biotite
14 monzogranite not different from the predominant facies of the northern pluton.
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17 The **Taipas** granitic stock is a small satellite (2 km²) located immediately to the
18 west of the Cantareira Granite, in the region between the northern and southern plutons
19 (Fig. 3c). The main rock type is a porphyritic biotite monzogranite usually more felsic
20 than the typical Cantareira granite, but it is compositionally diverse, and a facies similar
21 to the typical Cantareira porphyritic biotite monzogranite is locally present.
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24 The **Perus** tourmaline granites correspond to a series of small bodies of aplite-
25 pegmatite that occur in the neighborhood of Taipas and Cantareira northern pluton (Fig.
26 3c). These occurrences have attracted the attention of several researchers because of
27 their peculiar mineralogy, chemical composition (extremely fractionated; rich in several
28 incompatible elements as B, U and Rb) and structure (characteristically banded, with
29 alternating aplite and pegmatite bands) (Teupenheyer, 1994; Morteani et al., 2008).
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31 ***Sample petrography and geochemistry***

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33 Sample CANT-6, collected in the Basalto quarry, located at the westernmost
34 portion of the northern Cantareira Granite, is a typical porphyritic biotite monzogranite.
35 Sample MD-42b, collected in a roadcut in the Bandeirantes Highway (SP-348), is a
36 coarse-grained syenogranite from the southern Cantareira Granite, and is
37 petrographically and chemically similar to the Canivete facies described by Dantas
38 (1990).
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41 Sample TAP-1 from the Taipas stock was collected in the Pedreira Construcap, a
42 quarry located at the Av. Raimundo Pereira de Magalhães, Perus, close to the Basalto
43 quarry. It is a porphyritic biotite monzogranite with 2-3 cm K-feldspar megacrysts set in
44 a medium to coarse-grained matrix.
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1 The porphyritic samples from both Cantareira and Taipas are geochemically
2 very similar, with ~68% SiO₂, high K/Na, high Sr/Y and very fractionated chondrite-
3 normalized REE patterns without Eu anomalies (Fig. 4, 5). The coarse-grained
4 Cantareira syenogranite MD-42b is more evolved (72% SiO₂) and has lower Sr, but has
5 in common with the other two samples the high Sr/Y and fractionated REE patterns
6 without Eu anomaly.
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10 Pe-04 sample, representative of the Perus granites, was collected in a roadcut at
11 SP-21 Highway (Rodoanel Mario Covas). It is a medium-grained equigranular to
12 inequigranular tourmaline granite with banding defined by 1-2 cm thick tourmaline-rich
13 layers. It has a very evolved composition with 72% SiO₂, very low MgO, Ba and Sr and
14 high Y (40 ppm) and Rb/Sr (9). Its REE pattern is unfractionated with relatively high
15 contents of HREE and a deep negative Eu anomaly.
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25 *Zircon morphology and U-Pb dating*

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27 CANT-6 zircon crystals are 200-400 µm in length with aspect ratio 2:1 to 6:1.
28 Cores show oscillatory zoning; a few cores have convolute aspect; possible inherited
29 cores are small either light or dark in CL images; borders are typically oscillatory
30 zoned; dark rims are rare and very thin. Typical Th/U ratios are in the range 0.4-0.7
31 (average 0.5; three cores are exceptions with 1.6-1.7); average U is 308 ppm.
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36 Twelve points from CANT-6 zircons were analysed by Shrimp, and most are
37 <10% discordant (Table 3). Six points define a coherent age group, and allow obtain a
38 concordia age of **598.6±3.9 Ma** (Fig. 8). Three points not used in this regression yield
39 younger ²⁰⁶Pb/²³⁸U ages (479-571 Ma), which are attributed to high U, high ²⁰⁴Pb or
40 strong discordance (Table 3). Another three analyses have slightly higher ²⁰⁶Pb/²³⁸U
41 ages (606-612 Ma), are virtually concordant, and may correspond to antecrysts inherited
42 from early phases of the Cantareira Granite.
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49 MD-42b zircon crystals are relatively big (up to 500 µm in length) with 3:1 to
50 5:1 aspect ratios. They show oscillatory zoning with a general tendency to become
51 darker (U-rich) in CL images towards the border. In some cases, a homogeneous, wider
52 black border is present; usually, these crystals have CL-bright cores, suggesting that
53 they record a long history of magma evolution. Th/U are similar to those of CANT-6
54 zircons (0.3-0.7, average 0.54), but U (U 450-800 ppm average 575 ppm) and Th (150-
55 400 ppm, average 317 ppm) are higher.
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1 A concordia age of **591.9±3.7 Ma** (MSWD= 0.53, Fig. 7) was obtained from the
2 regression of LA-ICMS analyses of 24 spots from sample MD-42b, and is considered
3 the best estimate of its magmatic crystallization age. An inherited core with a
4 $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2.4 Ga, 21% discordant) shows oscillatory zoning, but differs from
5 the other crystals because it is included in a wide homogeneous zone that is light in the
6 CL images.
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10 TAP-1 crystals are 200-400 μm in length, with aspect ratio 3:1 to 6:1. Cores are
11 often unzoned and CL-bright images; one very bright core is corroded; borders are
12 oscillatory zoned, and thin dark rims are present in part of the crystals. Typical Th/U
13 ratios are in the range 0.5-1.0 (average 0.75; the corroded bright crystal has much lower
14 Th/U= 0.03); average U (corroded crystal excluded) is 202 ppm.
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20 Fourteen points were analyzed by Shrimp, and show significant discordance,
21 varying from 11 to 86% (Table 3). As shown by a Tera-Wasserburg plot, discordance is
22 related to excess ^{207}Pb , and the $^{206}\text{Pb}/^{238}\text{U}$ ages are homogeneous (Fig. 8). When two of
23 the most discordant analyses and one high ^{204}Pb point are discarded, the average
24 $^{206}\text{Pb}/^{238}\text{U}$ age of this sample is = **598.0±6.7 Ma** (MSWD= 1.3); this is considered the
25 best estimate of the magmatic crystallization age of TAP-1.
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31 No age determination was obtained for the Perus sample, which yielded only a
32 few zircon crystals that are strongly metamictic reflecting their high U content, and only
33 yield very discordant results. A U-Pb TIMS monazite result is reported in the literature
34 for this granite, but it consists of a single discordant fraction with a $^{207}\text{Pb}/^{206}\text{Pb}$ age of
35 ~580 Ma (Teupenheyer, 1994).
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42 *Zircon Hf isotope geochemistry*

43 The Hf isotope composition of zircons from the porphyritic biotite monzogranite
44 sample CANT-6 is just slightly more varied than those of ITQ-2 and MD-24 (5 ϵHf
45 units), and within the same range of $\epsilon\text{Hf}(t)$ (-20 to -15; average -16.9 ± 1.6) (Fig. 9).
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49 Zircons from inequigranular biotite syenogranite sample MD-42b have less
50 negative $\epsilon\text{Hf}(t)$, which do not overlap with the range of CANT-6 (-12 to -9.5; average -
51 11.1 ± 1.3), and are also very homogeneous, with a < 3 ϵHf units variation. A single
52 core with slightly more negative $\epsilon\text{Hf}(t)$ (-14.2) corresponds to a lighter portion with less
53 U.
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1 Zircons from Taipas TAP-1 porphyritic biotite monzogranite have also a small
2 spread of ε_{Hf} (3 units), and are slightly more negative than MD-24, but $\varepsilon_{\text{Hf}}(t)$ still do
3 not overlap with CANT-6 and samples from the Itaquí and Fazenda Itahyê (-14 to -10.5;
4 average -11.9 ± 1.2).
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7 Zircons from Perus tourmaline granite PE-4 have a similar spread (5 ε_{Hf} units);
8 at the assumed age of 598 Ma, their $\varepsilon_{\text{Hf}}(t)$ largely overlaps with those of CANT-6
9 ($\varepsilon_{\text{Hf}}(t) = -20$ to -16), but the average is lower (-18.5 ± 1.4) due to predominance of more
10 negative individual values.
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16 5.4. *Vila dos Remédios foliated quartz syenite*

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20 Sample JP-18 is an inequigranular coarse-grained quartz syenite with well-
21 developed foliation collected in a roadcut in the Fernão Dias Highway. The Vila dos
22 Remédios quartz syenite is metaluminous, and characterized by very low mg# (10),
23 high Zr (> 400 ppm), K/Na and Ba/Sr (~ 10) (Dantas, 1990), features that are more akin
24 to a within-plate geochemical signature.
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30 *Zircon morphology and U-Pb dating*

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33 Zircon crystals from JP18 show wide variations in shape, with aspect ratios 2:1
34 to 5:1, and lengths up to 300 μm (Supplementary File 3). CL images show white,
35 homogeneous elongated cores in many of the crystals with greater aspect ratios; thin
36 dark rims are present in a few crystals, mantling an inner zone with oscillatory zoning.
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40 LA-ICPMS analyses yield concordant results, but these spread over the
41 concordia over a large time range (636-510 Ma). The five points with ages lower than
42 570 Ma were discarded from regressions since they seem to correspond to regions
43 disturbed by the presence of inclusions or are otherwise too diverse from the main
44 population. Four CL-bright homogeneous cores yield the oldest ages, and are
45 interpreted as antecrysts; a regression from these points results in a concordia age of
46 630.5 ± 8.0 Ma (MSWD= 0.045). Two other crystals with inherited cores were analyzed
47 (20.1 and 22.1), but apparently the analyses included portions of younger rims, lowering
48 the dates. Regression of the remaining 13 analyses, mostly from rims and cores with
49 oscillatory zoning, resulted in a concordia age of **591.2 ± 3.4 Ma** (MSWD= 2.1), which
50 is considered the best estimate of the magmatic crystallization age of this sample.
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No Hf isotope data were obtained for sample JP-18.

5.5. *Tico-Tico Granite*

Sample petrography and geochemistry

Sample TICO-2 is a coarse-grained equigranular biotite-muscovite leucogranite with accessory garnet representative of the typical Tico-Tico Granite, collected in the Pedrix quarry near km 30 of the Bandeirantes Highway. It is a mildly peraluminous (ASI= 1.04) monzogranite with ~71% SiO₂, high K/Na and Ba/Sr, and a weakly fractionated REE pattern ((La/Yb)_N= 5) with a deep negative Eu anomaly ((Eu/Eu*)= 0.27)

Zircon morphology and U-Pb dating

TICO-2 zircon crystals are elongated and usually big (up to 500 µm in length), with aspect ratio 4:1 to 6:1. Cores show oscillatory zoning; a few small round cores may be inherited. Borders are typically oscillatory zoned and about 30% of the crystals have wide, dark (high U) rims in CL images. Typical Th/U ratios are in the range 0.1-0.5 (average 0.32); average U is 327 ppm.

Fifteen points were analyzed by Shrimp, and do not define a coherent age group, making the determination of the age of this sample a little tricky. Two discordant inherited cores were identified, with ²⁰⁷Pb/²⁰⁶Pb ages of 2113±26 Ma (point 10.1, 18% discordant) and 1739±22 Ma (point 12.1, 12% discordant); both have Neoproterozoic rims within the range of the other crystals. Points with <10% discordance have ²⁰⁶Pb/²³⁸U ages varying from 585 to 608 Ma, a range well outside uncertainty. A group of five samples with the lower ²⁰⁶Pb/²³⁸U ages yields a concordia age of **591.0±3.6 Ma**, with low MSWD (0.13) and a probability of concordance of 0.72 (Fig. 8). This is considered as the best estimate of the crystallization age of the Tico-Tico Granite. Three older virtually concordant grains with identical ²⁰⁶Pb/²³⁸U ages of 605-608 Ma, repeating the situation observed in CANT-6 sample from the Cantareira Granite; they may likewise correspond to antecrysts.

Zircon Hf isotope geochemistry

The Hf isotope composition of magmatic zircons from TICO-2 is remarkably homogeneous (a variation of is just 1.3 εHf units) and is within the range of the least

negative $\varepsilon_{\text{Hf}}(t)$ of all investigated samples (-12 to -10.5; average -11.2 ± 0.5) (Fig. 9). The two inherited grains have positive ε_{Hf} (+6.9 and +3.7) at their crystallization age.

6. Discussion

6.1. Age of granitic magmatism in the São Roque Domain

In this study, we have chosen for *in situ* U-Pb dating some of the typical and most expressive granite plutons from the SRD (Cantareira, Itaquí, São Roque). These are all predominantly formed by a similar rock type (high K, high Ba-Sr porphyritic (Hbl)-Bt monzogranite to granodiorite of metaluminous character, showing fractionated REE patterns with negligible Eu negative anomalies and high Sr/Y). To have a more complete sampling of the SRD granites, however, we also dated the most expressive occurrence of peraluminous leucogranites forming an independent pluton (Tico-Tico Granite) and granites with a subalkaline character, forming an independent pluton (Vila dos Remédios Quartz Syenite) or a small intrusive bodies within the Cantareira Granite (sample MD-42b).

All magmatic crystallization ages obtained here are within a small time range (from 604 ± 3 to 591 ± 4 Ma), independently of rock type. Taken separately, the high-K calc-alkaline granites are within an even smaller time range (604-595 Ma), and the ages obtained for the main rock type of the Itaquí, Fazenda Itahyê and Cantareira Granites are virtually indistinguishable considering the uncertainties. A slight age increase in the westernmost pluton (São Roque Granite) is also suggested by a U-Pb TIMS zircon date obtained in a rhyolite dike close to its northeast border (607 ± 7 Ma; single concordant fraction; Hackspacher et al., 2000). The subalkaline and peraluminous granites dated in this work (samples JP-18, MD-42b and TICO-2) occupy the younger part of this time range (all with ages ~ 591 -592 Ma), which in the case of the Cantareira Granite sample MD-42b is in agreement with the field relationships.

The absolute ages obtained in our study contradict the previous notion that the main period of granite emplacement in the SRD was ~ 630 -620 Ma, based on unpublished U-Pb TIMS zircon dating of the Cantareira, Itaquí, Tico-Tico (Topfner, 1996) and Barro Branco granites (Ragatky, 1998) and on a Shrimp date of 620 ± 11 Ma obtained by Tassinari et al. (2010) for the Moinho Granite. In our view, it is difficult to accept a 20-30 Ma lifetime for a structurally circumscribed pluton, even when it is

1 relatively voluminous and shown by detailed mapping to have been built through
2 several pulses such as Cantareira and Itaquí (Dantas, 1990; Wernick & Ferreira, 1993).
3 As suggested by recent precise dating of classical granite plutons in Sierra Nevada
4 batholith, up to 10 Ma is a more typical lifetime for plutons emplaced both in shallow
5 and intermediate-level crust (Coleman et al., 2004; Metzel et al., 2006).
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9 Zircon crystals showing ages slightly older than the magmatic ages were
10 identified in some of our samples (CANT-6, TICO-2, JP-18) and interpreted as
11 antecrysts. However, we did not find any evidence to confirm that the 630-620 Ma dates
12 obtained by Topfner (1996) correspond to magmatic crystallization ages. The fact that
13 the same discrepancy between Topfner's (1996) results and ours is observed in the
14 small and compositionally homogeneous Tico-Tico granite encourages us to look for
15 other reasons to explain how the TIMS determinations have resulted in older dates. Our
16 preferred explanation is that this is due to the incorporation, in the multi-grain zircon
17 fractions used by that author, of small, undetected inherited cores that had the effect of
18 slightly "aging" the final result. In fact, inheritance was clearly detected by Topfner in
19 both his Tico-Tico and Cantareira samples, and care was taken to avoid its influence on
20 the age estimate. However, as our CL images show, inherited cores, besides being
21 relatively abundant in some SRD granite samples, may be too small and thus impossible
22 to be detected or avoided during crystal selection for TIMS analyses, especially when
23 not supported by CL. These inherited cores are typically of Paleoproterozoic to Archean
24 age, and thus even small volumes may produce non-negligible shifts on the final
25 integrated TIMS age. This would also be reflected in an increase on the uncertainties of
26 the final dates, which is indeed observed in all ages reported by Topfner (1996) and
27 Ragatky (1998), which are above those expected for a precise technique such as TIMS.
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45 6.2. *Inferences on sources*

46 6.2.1 *Whole-rock geochemistry*

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48 I-type granites of HKCA affinity, largely predominant in the SRD, are much
49 abundant in the geological record, but their genesis and tectonic significance are still
50 very controversial (e.g., Roberts & Clemens, 1993; Chappell et al., 1998; Barbarin,
51 1999; Clemens et al., 2011; Castro, 2014). In particular, experimental results indicate
52 that more mafic "granitic" melts are not generated under typical conditions of partial
53 melting in the continental crust (e.g., Barbarin, 1999). Accordingly, I-type granitic rocks
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1 with SiO₂ <65% have been interpreted as products of diverse processes as fractionation
2 from basic magmas, mixing of basic magmas or their fractionates with felsic magmas
3 (Annen et al., 2006; Solano et al., 2012), entrainment of restite (Chappell et al., 1997,
4 1998) and/or peritectic minerals (Clemens et al., 2011) from the source or accumulation
5 from a more felsic melt (Miller & Miller, 2002)..
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9 The SRD HKCA granites are mostly <68% SiO₂, and often bear mafic
10 microgranular enclaves and synplutonic mafic dykes. These are unequivocal signals of
11 coeval mafic magmatism, but the extent to which these magmas were mixed and
12 incorporated into the granite magmas is unclear. Negative correlations of P and SiO₂
13 within individual plutons (e.g., Itaquí, Fig. 4) are consistent with apatite saturation over
14 the whole compositional range and would imply high *liquidus* temperatures if the
15 compositions of our granitic rocks with 64-70% SiO₂ are close to melts (960-1,000°C
16 using the apatite saturation curves of Harrison & Watson, 1984). Zircon saturation
17 temperatures from our HKCA granites in this silica range are much lower (770-790°C),
18 reflecting the zircon-undersaturated character of their parent melts.
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22 Other typical geochemical features of the SRD HKCA granites are the
23 fractionated REE patterns without negative Eu anomalies, high Sr and high Sr/Y ratios;
24 collectively, they are indicative that the parent melts were generated at relatively high
25 pressures, under conditions where plagioclase is unstable and garnet is stable. For
26 amphibolite protoliths, for instance, “Grt-in” requires minimum pressures of 15 kbar
27 (Moyen, 2009); this would imply melting in deep and probably thickened crust (e.g.,
28 Gromet & Silver, 1987), or even offcrust melting (see Castro, 2014).
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32 The peraluminous Tico-Tico Granite has all characteristics of being derived
33 from a purely crustal magma (e.g. SiO₂ >70%; peraluminous character; absence of
34 mafic microgranular enclaves). Its weakly fractionated REE patterns with negative Eu
35 anomalies and low Sr/Y indicate melting at lower pressure; the protolith is inferred to
36 have high time-integrated Rb/Sr to account for the high (0.717-0.725) ⁸⁷Sr/⁸⁶Sr(t).
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The zircon Hf isotope determinations presented in this study, the first reported
for the SRD granites, reveal significant variations that are important clues to inferences
on the magma sources. A more robust, but far from complete dataset of whole-rock Nd
isotope results exists in the literature, and it was complemented by six new

determinations in this work. Since the behavior of the Lu-Hf and Sm-Nd isotope systems in granitic rocks are often largely parallel, we discuss these results together.

The high spatial resolution of in situ techniques as LA-ICPMS and SIMS allows identification of chemical and isotope heterogeneity in zircon, which has been widely used to infer and quantify open-system processes in granitic magmas. A wide spread of $\epsilon\text{Hf}(t)$ within a single zircon crystal or among zircons from a single rock sample or thin section may result from magma mixing or contamination (Griffin et al., 2002; Kemp et al., 2007; Shaw & Flood, 2009) or indicate preservation of source heterogeneity (Farina et al., 2014).

Apart from obviously inherited cores with ages much older than the host granite, most samples studied here show comparatively small spread of $\epsilon\text{Hf}(t)$ (1σ of mean=1.2-1.5 ϵ units), slightly greater than analytical precision. Exceptions are the Tico-Tico granite, remarkably with an even more homogeneous Hf signature ($\epsilon\text{Hf}(t)=-11.5\pm0.5$) and the mafic microgranular enclave from Itaquí (with a spread of 11 $\epsilon\text{Hf}(t)$ units, from -11 to -22). Therefore, if sources of contrasting Hf isotope signature contributed to the magmas that produced our granites, they were efficiently homogenized before zircon crystallized. Evidence of mixing is clearly recorded only in the Itaquí microgranular enclave, where zircons that are morphologically, chemically and isotopically similar to those of the host granite ($^{176}\text{Lu}/^{177}\text{Hf}=0.0008$; mean $\epsilon\text{Hf}(t)\sim -18$) coexist with a distinctive population of CL-dark zircons that is more radiogenic ($\epsilon\text{Hf}(t)\sim -11$) and has much higher $^{176}\text{Lu}/^{177}\text{Hf}\sim 0.035$, indicative of crystallization from a HREE-rich melt.

In contrast to the scarce intra-sample dispersion, there is a marked variation of the mean zircon $\epsilon\text{Hf}(t)$ among the different granites, remarkably over the same range shown by the Itaquí enclave (from -22 to -11). Moreover, this has a clear geographic control, with an eastward shift to more radiogenic values over the short (~ 50 km) distance between the São Roque and Cantareira granites (Fig. 10a). Some granites from the easternmost region (Perus tourmaline granite and the typical HKCA Cantareira granite CANT-6) show intermediate values of $\epsilon\text{Hf}(t)$ (-18 to -16); the distinctiveness of this region is therefore the advent of granites with less negative $\epsilon\text{Hf}(t)$ (and correspondently lower Hf T_{DM}), represented by the non-typical HKCA samples from Taipás TP-1 and Cantareira (MD-42b) and the peraluminous, ferroan Tico-Tico Granite.

The Sm-Nd isotope data, for which a larger dataset is available, reveals a parallel behavior over the same spatial interval ($\epsilon\text{Nd}(t)$ from -14 in the São Roque Granite to -9

in Cantareira), confirming that the geographic variation shown by the Hf isotopes is meaningful (Fig. 10b). The Nd isotopic data allow expand the analysis of geographic variations to a wider E-W extension of ~150 km, thus encompassing most of the SRD. They show a return to more negative values ($\epsilon\text{Nd}(t) = -13$) east of Cantareira; this is followed by a jump to less negative to the east, where the least negative $\epsilon\text{Nd}(t)$ (-10 to -5) and corresponding lower Nd T_{DM} (1.6-1.4 Ga) of the whole domain occur (Ragatky, 1998). At the opposite side of the SRD (west of the São Roque Granite) lie the Sorocaba and São Francisco Granites, both of subalkaline affinity; published Sm-Nd isotope data (Dantas et al., 2000) show $\epsilon\text{Nd}(t)$ as negative as those of the São Roque Granite (Fig. 10b).

6.2.3. Inferences on sources from Hf and Nd isotopes

The Hf isotope signature of zircon from granites is a powerful tool to study the source(s) of their parent magmas, but extrapolation of ϵHf back to the time of protolith formation is strongly dependent on its (usually unknown) Lu/Hf ratio. This is well illustrated by the wide spread of depleted mantle “model ages” reported in Table 4. Zircons have extremely low $^{176}\text{Lu}/^{177}\text{Hf}$, with mean values typically varying in our samples from 0.0004 to 0.0008; these ratios usually correlate negatively with the degree of fractionation of the whole-rock REE patterns, reaching up to one order of magnitude higher values in the Perus tourmaline granite and in the more radiogenic crystals from the Itaquí mafic microgranular enclave. A Hf T_{DMz} , extrapolating the zircon $^{176}\text{Lu}/^{177}\text{Hf}$ back in time, will usually yield ages that are too young and only give a minimum limit for the crustal residence of Hf in the zircon (Andersen et al., 2002). The use of the whole-rock Lu/Hf, in a similar way to what is practice with the Sm/Nd isotope system, can yield more realistic model ages (Hf T_{DMwr}), but may carry comparatively greater uncertainty. In fact, even though of similar behavior and occupying the same sites in many minerals, Lu and Hf may be more commonly subject to fractionation compared to Sm and Nd, especially when minerals such as zircon and garnet control magma generation or evolution. We notice, anyhow, that Hf T_{DMwr} calculated for our samples compare well with whole-rock Nd T_{DM} , relative differences varying from +4 to -6%.

The following discussion on the sources of granite melts consider $^{176}\text{Lu}/^{177}\text{Hf}$ ratios commonly used in current literature, based on estimates for felsic crust (0.0093)

1 and intermediate crust (0.015) (Vervoort & Patchett, 1996; Vervoort & Blichert-Toft,
2 1999). Figures 11a and 11b are ϵ_{Hf} x time diagrams showing the $\epsilon_{\text{Hf}}(t)$ of the SRD
3 granites, and their calculated Hf T_{DM} for these two different $^{176}\text{Lu}/^{177}\text{Hf}$ ratios.
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5 Also plotted in Figure 11 are the calculated $\epsilon_{\text{Hf}}(t)$ of detrital zircons from SRD
6 metasediments (unpublished data from the authors, part of our ongoing study of zircon
7 provenance; cf. Henrique-Pinto et al., 2014). The detrital zircons spread a wide variety
8 of ages, from 3.4 to 1.7 Ga, the youngest zircons being coeval with the deposition of the
9 basal sequences, as inferred from intercalated metavolcanic rocks (the 1.76 Ga Morro
10 do Polvilho rhyolites). The distribution of zircon ages is not continuous; instead, it
11 shows some well-defined peaks at ~1.75, 2.1-2.2 Ga, 2.4-2.5 Ga and ~2.7 Ga, with
12 resulting gaps. The widest gap spans ca. 0.3 Ga, and separates the latest rock-forming
13 event recorded in the continental source (inferred to be the São Francisco Paleoplate;
14 Henrique-Pinto et al., 2014) from the within-plate volcanism associated with rifting that
15 initiated the deposition of the SRD sequences, later evolving to a passive-margin
16 environment. Protoliths with positive $\epsilon_{\text{Hf}}(t)$ (inferred to be “juvenile”) were
17 predominant in the 2.4-2.5 Ga sources of the SRD metasediments. Zircons from the
18 younger event at 2.1-2.2 Ga show a continuous range of $\epsilon_{\text{Hf}}(t)$ (+2 to -13) and are
19 mostly compatible with reworking of the juvenile crust generated at 2.4-2.5 Ga. The
20 youngest detrital zircons, broadly coeval with the basin formation, are much less
21 abundant, have very negative $\epsilon_{\text{Hf}}(t)$ (-8 to -20), and are thus inferred to come from
22 protoliths generated from reworking of continental crust.
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24 If the SRD granites derived from protoliths following a path corresponding to
25 the $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ curve (Figure 11a), then all sources of detrital zircons with ages
26 >2.5 Ga, and also those more negative in the 2.1-2.2 Ga population (with $\epsilon_{\text{Hf}}(t) < -6$)
27 would be too negative at 600 Ma to be the only component even of the more
28 unradiogenic São Roque Granite (average $\epsilon_{\text{Hf}600} = -23$). If these protoliths contributed to
29 the SRD granites, participation of other more radiogenic source(s) is required. On the
30 other hand, 2.4-2.5 Ga “juvenile” protoliths and those possibly resulting from reworking
31 of this crust at 2.2-2.1 Ga would have the appropriate $\epsilon_{\text{Hf}600}$ to generate most of the
32 SRD high-K calc-alkaline granites.
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34 The group of SRD granites with more radiogenic $\epsilon_{\text{Hf}600}$, comprising the Taipas
35 stock and the two non-calc-alkaline samples (Tico-Tico Granite and MD-42B
36 Cantareira syenogranite), cannot be derived from any of the >2.1 Ga potential sources.
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1 The detrital ~1.75 Ga zircon population has protoliths resulting from recycling of older
2 crust, and is also too negative to represent the protoliths of these granites. On the other
3 hand, the two inherited zircons from the Tico-Tico Granite with ages ~2.1 and 1.7 Ga
4 and positive $\epsilon\text{Hf}(t)$ may fill the requirements for the sought source. The fact that these
5 zircons occur as inherited cores in the Tico-Tico Granite is a strong argument in favor
6 of the hypothesis that they may derive from the protolith of this granite. Moreover, this
7 is suggestive that although not identified so far in the detrital zircon assemblage of
8 coeval sedimentary deposits, new crust was generated in the SRD at ~2.1-1.8 Ga, and
9 may be an important component of it. In this respect, we call the reader's attention to
10 the $\epsilon\text{Hf}(t)$ of the 1.76 Ga Morro do Polvilho Rhyolite that is more radiogenic than those
11 of the coeval detrital zircons, with one grain plotting close to the Tico-Tico inherited
12 crystal (Fig. 11).
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22 Figure 11b compares the picture just described with what would result if the
23 SRD granites derived from more felsic protoliths following a path corresponding to the
24 $^{176}\text{Lu}/^{177}\text{Hf} = 0.093$ curve. Hf T_{DM} are lowered by 300-400 Ma, and virtually no overlaps
25 with the evolutionary paths of the detrital zircon assemblage would occur, even for the
26 more unradiogenic granite sample. This would then require a much greater participation
27 of younger sources that were more radiogenic at ~600 Ma and were not sampled in the
28 detrital zircon assemblage.
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34 At this point, it is important to point out that “juvenile” sources with ages <1.5
35 Ga are a potential component in all SRD granites. A mantle contribution from basic
36 melts at the time of granite generation (600 Ma) would be consistent with both
37 compositional and thermal requirements, mostly for the petrogenesis of the more mafic
38 HKCA granites (see below). However, the isotope signature of this mantle component
39 is yet poorly constrained, and may be that of an “enriched” rather than depleted or
40 primitive mantle, as suggested for mantle-derived magmas in neighbor domains from
41 the Ribeira Belt (e.g., Janasi et al., 1993; Carvalho et al., 2014). The presence of a
42 zircon population with distinctly less negative ϵHf_{600} in a basic (50% SiO_2) enclave
43 from the Itaquí Granite is consistent with the need for a mantle contribution, but it is
44 still too negative (-10), implying previous mixing with old crust or derivation from an
45 enriched mantle.
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56 The Nd isotope dataset is consistent with our findings from Hf isotopes.
57 Although the negative ϵNd_{600} indicate sources with long crustal residence for all studied
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granite plutons, the observed range is more radiogenic than the values calculated at their crystallization age for both the Mesoproterozoic (1.5-1.8 Ga) passive-margin metavolcano-sedimentary sequences of the São Roque Domain and their inferred Archean to Paleoproterozoic continental sources (Fig. 12). Therefore, a contribution from sources with less negative ϵNd_{600} is also required to explain the observed pattern.

6.3. *Tectonic implications*

In his classic review paper on granite classification and its links with geodynamic environments, Barbarin (1999) emphasized that “first of all, a granitoid can be used as a geodynamic indicator only when it is correctly typed and also precisely dated. It is also clear that granitoids should not be used alone but in association with structural data” The reevaluation of the main period of granite magmatism in the SRD implied by our new in situ U-Pb dating results illustrates this point. In spite of their structural and compositional characteristics more akin to those of the “post-tectonic” “Caledonian I-type” granites of Pitcher (1983) recognized in early reviews (Janasi & Ulbrich, 1991), overlap of ages with supposedly “syn-orogenic” granites from neighbor domains has led many authors in recent literature to relate the SRD HKCA granites with a continental arc geodynamic environment. The main age range established in the present work for these granites (605-595 Ma) allows a temporal correlation with the “late-orogenic” magmatism in the neighbor Açungui Domain (e.g., Leite et al., 2007), and is consistent with their emplacement after the metamorphic peak and any known indications of high-pressure metamorphism (e.g., Reno et al. 2009, Campos Neto & Caby, 1999). In this sense, the SRD granites can be related to a “post-collisional” or, more conservatively, a late deformation tectonic setting.

However, this does not imply that the SRD HKCA granites are disconnected from the voluminous calc-alkaline granite magmatism that immediately preceded them in the neighbor domains of the Ribeira Belt. Indeed, the main period of batholith construction in neighbor domains seems just slightly older in the Açungui Domain (620-610 Ma; Janasi et al., 2001; Leite et al., 2007; Prazeres Filho et al., 2005) and in the Socorro-Guaxupé Nappe (630-620 Ma; Janasi, 1999 etc). Notably, the main granite type forming these batholiths is equally a high-K calc-alkaline granite, and their temporal link to convergent tectonics and a magmatic arc environment is unclear at best. To cite Barbarin (1999) again, “high-K calc-alkaline granites and granodiorites are

1 present in various geodynamic environments. They actually indicate more a variation of
2 the tectonic regimes than a specific geodynamic environment. KCG [his “K-rich and K-
3 feldspar porphyritic Calc-alkaline Granitoids”] occur either during periods of relaxation
4 that separate periods of culmination within a collision event, or transition from a
5 compressional regime to a tensional regime”. Their K-rich and CaO-poor compositions
6 (compared to arc-related calc-alkaline granitoids) are interpreted to reflect the
7 predominance of a crustal component, which is clearly demonstrated from the isotope
8 data for the SRD granites and other HKCA granites from the Ribeira Belt. In this
9 respect, it is illustrative to recall that many authors advocate that voluminous “post-
10 collisional” high-K granite magmatism is typical of intracratonic orogenic belts (e.g.,
11 Liégeois et al., 2013) that may lead to strong reworking of a formerly stable area, and
12 ultimately to the formation of a “metacraton”. HKCA granites are recognized as major
13 products of the Neoproterozoic events in both the Ribeira and Borborema Provinces of
14 east Brazil, which led some authors in recent years to advocate an intracontinental
15 origin and a role on the partial destruction of former cratonic areas (Silva et al., 2005;
16 Ganade de Araujo, 2014; Neves, 2015; Meira et al., 2015).

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18 In the Ribeira Belt of south Brazil, even if a large proportion of HKCA granites
19 are revealed as “post-collisional”, there is good evidence that they were preceded by a
20 prolonged stage of arc magmatism related to ocean closure (~800-650 Ma; Tupinambá
21 et al., 2012; Hackspacher et al., 2005; Heilbron et al., 2008). In this context, the HKCA
22 magmatism would be better explained as a product of transformation of a former active
23 margin by collisional processes. The assessment of the characteristics and relative
24 contributions from old continental sources and younger “juvenile” material to the
25 Neoproterozoic granite magmatism over time and space along the province is central to
26 resolve the geodynamic setting. One important finding of the present work is that,
27 although the SRD granitic magmas may largely derive from protoliths related to
28 passive-margin metavolcano-sedimentary sequences and their inferred Archean to
29 Paleoproterozoic continental sources, a component with less negative ϵ_{Nd} and ϵ_{Hf} at
30 600 Ma is required. This source may be inferred to become more important eastward
31 and appears to have been sampled at shallower crustal levels after a period of HKCA
32 magma generation at high temperatures and great depths. A similar behavior seems to
33 exist in the neighbor Açungui (Janasi et al. 2014) and Socorro-Guaxupé (Janasi, 1999,
34 2002) domains, suggesting an asymmetry that could be connected to the presence of an

oceanic margin to the east-southeast, in agreement with the proposed presence of magmatic arc terranes SE of the Embu Terrane (Fig. 1).

7. Conclusions

In situ U-Pb dating (Shrimp and LA-ICPMS) of the main granite plutons from the central São Roque Domain indicates that they were all emplaced within a short time interval (~605-590 Ma) that is ca. 30 Ma younger than suggested by previous literature data obtained by TIMS. The discrepancy might be related to the presence of small inherited cores that are difficult to separate and even to detect in multi-grain fractions used for those TIMS studies.

A few inherited cores dated by in situ techniques have slightly to moderately discordant ages that are consistent with the age range found in the detrital zircons from metasediments of the São Roque Domain (1.7-3.3 Ga, with predominance of ~2.1-2.2 Ga). This suggests that the main protoliths for the Neoproterozoic granite magmas can be equivalent to those inferred for the ~1.75-1.4 Ga SRD detrital metasediments, which derived from continental sources mainly of Paleoproterozoic age in continental rift and passive margin environments.

The Hf and Nd isotope signatures of the Neoproterozoic granite magmas, obtained respectively from zircon in situ and whole-rock analyses, are also consistent with sources with a prolonged crustal residence. The Hf isotopes, in particular, point to the predominance of Paleoproterozoic sources which were juvenile at ~2.4-2.5 Ga, and partially reworked at 2.1-2.2 Ga. However, sources more radiogenic than these at 600 Ma are required to explain the less negative ϵ_{Hf} and ϵ_{Nd} of several SRD granites, especially those of peraluminous and subalkaline character. Inherited cores from the Tico-Tico leucogranite reveal that these sources could correspond to juvenile crust accreted during the ~1.75 Ga rifting event that initiated the deposition of the supracrustal sequences or even during the latest (~2.1 Ga) events recorded in the SF craton. Such sources are unexposed and were not detected in the detrital zircon assemblage of the SRD metasediments.

Although not apparent from the Hf-Nd isotope signatures, a Neoproterozoic juvenile (mantle-derived) component may be present, at least in the more primitive granites, which show field evidence of mingling with basic melts and are too mafic to

correspond to pure crustal melts. Data from regional studies of Neoproterozoic magmatism indicate that this component probably corresponds to enriched mantle, and therefore it could have negative ϵ_{Hf} and ϵ_{Nd} , and thus would not shift dramatically the signatures of the granite magmas.

Paradoxically, the more unradiogenic Hf and Nd signatures are shown by the predominant HKCA granites, which derived from higher temperature melts generated at great depths (>30 km), as indicated by high Sr/Y and fractionated REE patterns with weak to absent Eu anomalies. Within the central SRD, an eastward shift to less negative ϵ_{Hf} and ϵ_{Nd} seems associated with melting of sources with less crustal residence time at shallower depths. It is not yet clear if this pattern simply reflects a rise of a thermal anomaly in a short period of time or whether, as suggested in some recent regional studies, these more juvenile sources become a more voluminous component of the crust in that direction.

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Figure captions

Figure 1. Tectonic framework of SE Brazil with location of the São Roque Domain in the Ribeira Belt. AçT= Açungui Doman; CFT= Cabo Frio Terrane; CT= Curitiba Terrane; ET= Embu Terrane; Go= Goiás Magmatic Arc; LAM= Luiz Alves Microplate; OcT= Ocidental Terrane; OrT= Oriental Terrane; SBB= South Brasilia Belt; SGN= Socorro-Guaxupé Nappe; SRD= São Roque Domain

Figure 2. Geological sketch of the São Roque Domain showing the main granite occurrences along which their U-Pb ages, $\epsilon\text{Nd}(t)$ and $\epsilon\text{Hf}(t)$.

Figure 3. Geochemical variation diagrams for selected granite occurrences from the SRD, showing the compositions of samples analyzed in this study.

Figure 4. Chondrite-normalized (Boynnton, 1984) REE patterns of granites from the SRD: (a) high-K calc-alkaline granites; (b) other granite types.

Figure 5. Variations of $^{87}\text{Sr}/^{86}\text{Sr}(t)$ of SRD granites versus (a) $^{87}\text{Rb}/^{86}\text{Sr}$ and (b) $\text{Sr } T_{\text{DM}}$.

Figure 6. Maps of individual granite occurrences (a) São Roque (from Andrade et al., 1990), (b) Itaquí (from Wernick & Ferreira, 1993), (c) Cantareira (from Dantas, 1990), showing our new U-Pb ages, $\epsilon\text{Nd}(t)$ and $\epsilon\text{Hf}(t)$.

Figure 7. U-Pb isotope diagrams showing results of in situ zircon dating by LA-ICPMS.

Figure 8. U-Pb isotope diagrams showing results of in situ zircon dating by Shrimp.

Figure 9. $\epsilon\text{Hf}(t)$ results of *in situ* analyses of zircons from SRD granites. Results correspond to individual analyses, ordered from least (left) to more negative values. Horizontal scale is the same for all samples to permit visualization of within-sample spreads. Whole-rock $\epsilon\text{Nd}(t)$ for selected granites (right-hand scale) shown for comparison.

Figure 10. Geographic variation (in UTM eastings) of (a) average zircon $\epsilon\text{Hf}(t)$ and (b) whole-rock $\epsilon\text{Nd}(t)$ for the SRD granites.

Figure 11. $\epsilon\text{Hf} \times \text{time}$ diagram for SRD granites based on results for individual *in situ* analyses of zircon crystals. Extrapolation of evolution curves to times before granite generation were calculated to $^{176}\text{Lu}/^{177}\text{Hf}$ ratios corresponding to (a) “intermediate” (0.015) and (b) “felsic” crust (0.0093) (see text). Also shown for comparison are Hf isotope data for detrital zircons of metasediments from western (Voturuna) and central (Jaraguá and Pirucaia) portions of the SRD, as well as for the ~1.75 Ga Polvilho meta-rhyolite (unpublished data from the authors).

Figure 12. Whole-rock $\epsilon\text{Nd} \times \text{time}$ diagram for SRD granites. Values for the São Francisco Granite from (Dantas et al. (2000) and for granites from the eastern portion of the SRD from Ragatky (1998). Nd isotope data for SRD metasediments and granite pebbles from SRD metaconglomerates are from Henrique-Pinto et al. (submitted to Journal of South American Earth Sciences) and Henrique-Pinto et al. (2010), respectively.

Tables

Table 1. Results of whole-rock Sr and Nd isotope determinations in SRD granites.

Table 2. Results of U-Pb dating of SRD granites by Shrimp.

Table 3. Results of U-Pb dating of SRD granites by LA-ICPMS.

Table 4. Results of LA-ICPMS in situ Hf isotope determinations in zircon crystals from SRD granites.

Supplementary material

SM-1. Full description of analytical methods.

SM-2. Whole-rock composition of granite samples selected for this study.

SM-2. Chatodo-luminescence images of zircons studies in this work, with location of spots and results of U-Pb dating and ϵ Nd isotope determinations.

Supplementary File 1. Analytical Methods

1. Whole-rock major and trace-element analyses

X-ray Fluorescence was used to determine the major, minor and trace elements in whole rock samples. Large samples typically weighing 6-8 kg were broken into pieces of about 3-5 cm using hammer or hydraulic press, and then were crushed to fragments with an average size of 1.5 cm with a jaw breaker of Mn-steel. The material was then split in a cross-type Jones splitter, yielding 100-150 g sub-samples representative of the starting material. The sub-samples were then milled for 15 minutes on a Pulverisette-type planetary agate mill. This overall time is usually enough for the material to reach a particle size smaller than 200 mesh.

Analyses were performed in a Phillips PW2400 spectrometer at the NAP-Geonalitica, Instituto de Geociências, Universidade de São Paulo, Brazil, following the protocol described in Mori et al. (1999). Major and minor elements were analyzed from molten tablets obtained from 1g sample and 9 g of a mixture of spectroscopic grade lithium tetra and metaborate at 1100-1200° C in a platinum crucible, using a Claisse fusion machine. Trace elements were analyzed from pressed pellets obtained from homogenization of the pulverized sample (previously micronized in a McCrone Micronizer) and pressing to 30 ton. with wax. Analytical quality was controlled using a reference material granite JG-1a from Geological Survey of Japan as an unknown sample, and duplicated samples. The values obtained should be within 2σ of the certified values, and the duplicated samples within 1% of variation.

Rare earth and other trace elements were determined by ICPMS in a Thermo-Analitica ICAP quadrupole analyzer at the NAP-Geonalitica, Instituto de Geociências, Universidade de São Paulo, Brazil, following the protocol described in Navarro et al (2008).

Approximately 40mg of rock powder with grain size<200 mesh were placed in a Teflon capsule Parr bomb and added with 5 ml of nitric acid and 15 ml of HF, both sub boiling distillates. The material is heated to 200° C in an electric oven, under pressure, for five days. The material is then cooled and transferred to a PFAbeaker where the solution is heated in hot plate; in this process, SiF₄ is eliminated by evaporation. After drying, the material is dissolved and transferred to a plastic bottle where weights were adjusted to 100g with 1% HNO₃. Analytical quality control was checked by the analyses of reference materials JG-1a and JR-1 as unknown samples, blank and duplicate of some samples. The values obtained should be within 2σ of the certified values, and the duplicated samples within 1% of variation (Navarro et al, 2008).

2. Whole rock Nd and Sr isotope ratios

Rb-Sr isotopic analyses of whole rock samples were performed at CPGeo, Instituto de Geociências, Universidade de São Paulo, Brazil, following the protocols described by Sato et al (2008). The attack of the samples is similar to that used for ICP-MS, the main difference is the greater digestion time (10 days at 160 ° C) in a Parr bomb. Element separation in columns loaded with cation exchange resin AG-50W-X8 (200-400mesh) used deionized water and sub-boiling HCl in varying concentrations. Sr extraction was performed with 2.5N HCl, and the residue of this phase was washed with 6.2N HCl for

subsequent extraction of the REE. Samarium and Neodymium were extracted from columns filled with Teflon powder and successive washes with 0.26N HCl for Nd separation and 0.55N HCl for Sm.

Sr isotope analyses were performed in mass spectrometer of thermo ionization (TIMS) model TRITON of Thermo Scientific; Nd analyses were performed in the mass spectrometer with inductively coupled plasma, model Neptune of Thermo Scientific. Absolute concentrations of Sm and Nd concentrations were determined from separate analyses by ICPMS; Rb and Sr were determined by XRF.

Normalizing ratios were $^{86}\text{Sr}/^{87}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and decay constants are those from Steiger & Jaeger (1978) and Michard et al (1985) for Sr and Nd, respectively. In the period of analyses, Nd blank was 61 pg and Sr blank was 142 pg. External reproducibility of Sr was checked by analyses of standard reference material NBS-987 from NIST-USA and in the period 09/2013 to 08/2014 has yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710243 ± 0.000024 , compared to a NIST certified value of 0.71034 ± 0.00026 . External reproducibility of Nd was checked by analyses of standard reference material JNdi-1 (Tanaka, 2000) and in the period 11/2013 to 10/2014 has yielded an average $^{143}\text{Nd}/^{144}\text{Nd}$ 0.512097 ± 0.000005 . For calculation of epsilon Nd, CHUR values were $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$ and $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$ (Hamilton et al, 1983)

3. Zircon concentration, mounting and cathodoluminescence study

The separation and concentration of zircon consists of crushing, grinding, sieving, vibrating table, electromagnetic separation, heavy liquids and finally manual picking. The routine used at CPGeo is described by Sato et al (2014) and consists of the following steps: a) rock samples (0.5 to 3 kg for granites and ~ 20 kg for mafic rocks) is crushed in a jaw crusher; b) crushed material is screened to separate a fraction of 100-250 mesh particle size, using a disk mill and a battery of sieves; c) the separated fraction is taken to a vibratory table to concentrate heavy minerals; d) magnetic minerals are removed with a hand magnet; e) minerals with different magnetic susceptibilities are concentrated in a Frantz-type magnetic separator, by varying the inclination and the intensity of the electromagnetic field; f) the least magnetic fractions are passed successively into bromoform ($d = 2.85 \text{ g/cm}^3$) and methylene iodide ($d = 3.2 \text{ g/cm}^3$) to further concentrate the heavy minerals of interest. Any remaining sulfides present in the concentrates are eliminated with HCl or HNO_3 . About 50-100 zircon grains are separated by hand picking with the aid of a magnifying microscope, and then mounted on double sided adhesive tape and embedded in epoxy-typeresin. The mount is then polished to expose the fresh surface of the grain trapped in the resin.

A previous study of cathodoluminescence (CL) of each of the samples was necessary to choose the proper position of the spot during the in situ analyses by Shrimp or LA-ICPMS. After a thin layer of gold cover (2-3nm) was added to the mounts, these images were obtained in a FEI Quanta 250 SEM spectrometer with a XMAX CL detector (Oxford Instruments). Operating conditions were: high voltage, 15 kV, distance, 16.9-17 mm, PMD detector, range of magnification, 95-250x.

4. U-Pb geochronology by Shrimp and ELA-ICPMS

Part of the U-Pb zircon dating was performed in the SHRIMP IIe equipment installed at CPGeo, Instituto de Geociências, Universidade de São Paulo. The Shrimp is a mass spectrometer coupled to a high resolution ion microprobe that uses a collimated and accelerated beam of primary ions (O_2) to reach a target where secondary ions are generated from 30 μm spots. The secondary ions are accelerated through the equipment and the isotopes generated by the sample, $^{254}UO^+$, $^{206}Pb^+$, $^{207}Pb^+$, $^{208}Pb^+$, $^{238}U^+$ and ^{254}ThO and $^{196}Zr_2O^+$, are measured successively. The corrections required by the technique are made by the analyses of unknown materials and reference materials with known isotopic ratios (matrix-matched) for determining specific calibration factors (Black et al, 2004). 12-16 spot analyses from each of the unknown zircon samples are performed according to the method described in Sato et al (2014). During the run every 5 determinations analyzed the Temora-2 reference material (estimated age 416.78 ± 0.33 Ma; Black et al, 2004) is used as $^{206}Pb/^{238}U$ age reference, for calculation of common Pb correction factors and fractionation factors. Common lead corrections usually use ^{204}Pb according to Stacey and Kramer (1975). Reference material SL13 (238 ppm) is used as U composition reference. Data are reduced with SQUID 1.6 software (Ludwig, 2009) and ISOPLOT 4 (Ludwig, 2003) has been used for treatment of data to estimate ages and generate diagrams.

The determinations by ELA-ICPMS (Excimer Laser Ablation - ICPMS) were also held on the premises of CPGeo, Instituto de Geociências, USP and used the Excimer Laser pulsed 193nm ArF (Photon Machine) with operating conditions 6 mJ, $8.55 J/cm^2$ (100%), 6 Hz and 32 μm spot. The ablated material was carried through an Ar and He flow of 0.9 L/min to a HR-ICPMS multicollector spectrometer, Neptune model from Thermo-Finnigan, operated at 926W. A mixed configuration of Faraday collectors for readings in Volts and ion multipliers (MIC's) for readings in cps allowed to obtain simultaneous measurements of ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U , ^{204}Hg and ^{202}Hg . The signal obtained for each of the isotopes is integrated over 60 s laser ablation at each point analyzed. Two worksheets were obtained with 13 determinations each, interspersed by 2 analyses of blank for ^{204}Pb correction, 2 determinations of zircon reference material GJ-1 (estimated $^{206}Pb/^{238}U$ age of 599.8 ± 4.5 Ma; Jackson et al, 2004) to correction of the U/Pb and Th/U ratios and 2 determinations of Nist-612 for correction of the $^{204}Pb/^{206}Pb$ ratio.

5. Hf isotope analyses in zircon by LA-ICPMS

Zircon Hf isotope analyses were performed using a HR-ICPMS multicollector spectrometer, Neptune model from Thermo-Finnigan attached to ArF Excimer Laser 193 nm (Photon Machine) with operating conditions 6 mJ, $8.55 J/cm^2$ (100%), 7 Hz and 47 μm spot size. The ablated material was loaded into the plasma operated at 1000 W, through an Ar flow of 0.5 L/min, 0.25 L/min of He and 1.2 L/min of N_2 . The collector configuration allowed simultaneous measurements of the isotopic ratios $^{173}Yb/^{171}Yb$, $^{179}Hf/^{177}Hf$, $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$. The measured values of the $^{176}Hf/^{177}Hf$ ratio for the GJ-1 reference material were 0.282063 ± 0.000293 ($N=4$, 2σ), in agreement with the value 0.282000 ± 0.000004 by Morel et al. (2008). The results were processed in Excel spreadsheet using the ^{176}Lu decay constant = $1.867e-11$ (Soderlund et al., 2004).

Present-day ratios $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$ (CHUR) and 0.283225 (DM); $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$ (CHUR) 0.038512 (DM) were used for calculations of εHf . Double-stage Hf model ages were calculated using values from literature for different reservoirs (see text).

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Figure 1

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Figure 12

MD-24

Table 1

sample	pluton	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd (calc.)	¹⁴³ Nd/ ¹⁴⁴ Nd (meas.)	error (2σ)	εNd 0	εNd t=600	fSm/Nd	Nd TDM (Ma)
SR-07	São Roque	8.37	48.4	0.105	0.511506	0.000005	-22.1	-15.0	-0.47	2152
SR-05	São Roque	3.25	15.5	0.127	0.511620	0.000008	-19.9	-14.5	-0.36	2511
ITQ-2	Itaqui	7.09	40.8	0.105	0.511660	0.000006	-19.1	-12.1	-0.47	1941
TAP-01	Taipas	5.2	29.9	0.105	0.511775	0.000006	-16.8	-9.8	-0.47	1780
MD42B	Cantareira	3.64	22.5	0.098	0.511791	0.000005	-16.5	-9.0	-0.50	1645
MD24	Faz. Itahyê	7.89	44.7	0.107	0.511716	0.000006	-18.0	-11.1	-0.46	1890
sample	pluton	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr (calc.)	⁸⁷ Sr/ ⁸⁶ Sr (meas.)	error (2σ)	εSr t=600	⁸⁷ Sr/ ⁸⁶ Sr t=600	Sr TDM (Ma)	
SR-07	São Roque	136	754	0.521	0.717304	0.000056	129	0.71285	2206	
SR-05	São Roque	158	202	2.272	0.730245	0.000052	99	0.71080	880	
ITQ-2	Itaqui	100	763	0.380	0.713538	0.000054	92	0.71029	2357	
TAP-01	Taipas	141	641	0.637	0.714671	0.000055	77	0.70922	1467	
MD42B	Cantareira	149	474	0.912	0.716983	0.000042	76	0.70918	1188	
MD24	Faz. Itahyê	119	858	0.400	0.712867	0.000058	80	0.70945	2092	

Sm and Nd (ppm) by solution ICPMS; Rb and Sr (ppm) by XRF
initial ratios calculated at t= 600 Ma

Table 2

Shrimp data

Sample Spot	Pb total (common) %	Pb rad ppm	Th ppm	U ppm	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	% err	²⁰⁷ Pb/ ²³⁵ Pb	% err	²⁰⁶ Pb/ ²³⁸ Pb	% err	²⁰⁸ Pb/ ²⁰⁶ Pb	% err	Rho	²⁰⁶ Pb/ ²³⁸ U	1 σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1 σ	²⁰⁸ Pb/ ²³² Th	Age (Ma)	1 σ	Discor-dant	
Tico-Tico Granite TICO-2																							
UTM S: 7413075 x 318718, 23 K																							
1.1	0.05	29.6	117	374	0.3	0.061	1.0	0.810	1.1	0.092	0.6	0.095	1.9	0.027	2.0	0.53	567	3	652	22	533	11	15
2.1	0.13	32.8	44	394	0.1	0.059	1.1	0.817	1.0	0.097	0.4	0.034	2.6	0.029	2.8	0.46	596	3	584	25	529	24	-2
3.1	0.21	22.5	103	265	0.4	0.059	1.7	0.853	1.2	0.099	0.5	0.119	1.7	0.029	1.8	0.44	605	3	566	38	560	15	-6
4.1	0.25	21.0	88	251	0.4	0.059	2.2	0.812	1.4	0.098	0.9	0.113	1.8	0.030	2.1	0.63	599	5	558	48	577	20	-7
5.1	-0.16	21.3	160	255	0.6	0.063	1.1	0.818	1.2	0.097	0.5	0.200	1.4	0.030	1.5	0.44	600	3	693	23	611	9	16
6.1	0.62	33.1	140	403	0.4	0.061	2.2	0.823	1.2	0.095	0.4	0.119	1.4	0.032	1.5	0.36	586	2	632	49	561	18	8
7.1	0.08	23.4	126	276	0.5	0.059	1.4	0.844	1.2	0.099	0.5	0.140	1.6	0.029	1.7	0.42	606	3	570	30	578	11	-6
8.1	0.32	19.5	80	235	0.4	0.059	1.3	0.832	1.2	0.096	0.5	0.106	1.9	0.029	2.1	0.45	591	3	568	29	542	12	-4
9.1	0.35	17.9	88	280	0.3	0.061	1.8	0.608	1.5	0.074	0.5	0.112	1.9	0.025	2.1	0.34	460	2	633	38	473	13	38
10.1 ^(*)	0.07	78.0	100	284	0.4	0.131	0.7	5.737	1.2	0.319	1.0	0.110	1.0	0.097	1.5	0.82	1789	16	2117	13	1839	30	18
10.2	-0.02	45.6	61	549	0.1	0.061	0.8	0.649	3.2	0.095	0.4	0.066	1.7	0.055	1.9	0.12	595	2	654	16	1095	19	10
12.1 ^(*)	0.11	68.1	124	289	0.4	0.106	0.6	4.167	0.7	0.275	0.4	0.123	1.0	0.076	1.1	0.61	1559	6	1739	11	1449	20	12
12.2	0.05	32.7	46	385	0.1	0.059	1.2	0.822	1.0	0.099	0.4	0.037	2.6	0.029	2.7	0.45	608	3	575	25	566	24	-5
13.1	0.05	29.3	82	356	0.2	0.060	1.2	0.796	1.0	0.096	0.5	0.073	1.9	0.030	2.0	0.45	590	3	598	26	582	15	1
14.1	0.17	21.5	48	315	0.2	0.060	1.2	0.638	1.4	0.079	0.5	0.057	2.5	0.029	2.6	0.36	492	2	602	26	531	16	22
Cantareira Granite CANT-6																							
UTM S: 7409165 x 323786, 23K																							
concordia age: 598.6±3.9 Ma																							
1.1	0.06	20.1	90	242	0.4	0.061	1.1	0.819	1.2	0.097	0.5	0.120	1.9	0.030	2.0	0.43	595	3	652	44	594	18	10
2.1 ^(*)	0.80	33.8	245	494	0.5	0.060	1.4	0.659	1.5	0.079	0.4	0.173	1.2	0.027	1.2	0.26	490	2	578	59	481	13	18
3.1	-0.05	28.7	163	335	0.5	0.061	0.9	0.835	1.0	0.100	0.5	0.154	1.4	0.031	1.5	0.44	612	3	638	23	614	10	4
4.1	0.06	31.0	175	364	0.5	0.062	0.9	0.846	1.0	0.099	0.4	0.150	1.4	0.030	1.5	0.43	609	3	601	23	592	9	-1
5.1	0.29	14.7	97	176	0.6	0.063	1.3	0.848	1.4	0.097	0.6	0.171	2.3	0.029	2.4	0.44	598	4	567	56	565	18	-5
5.2	0.17	29.3	254	351	0.7	0.065	1.2	0.875	1.3	0.097	0.5	0.221	1.2	0.029	1.3	0.36	597	3	583	37	563	9	-2
6.1 ^(*)	0.16	12.3	227	145	1.6	0.068	1.8	0.938	2.0	0.099	0.8	0.486	1.2	0.030	1.5	0.39	606	4	607	45	586	9	0
7.1	0.14	10.6	210	128	1.7	0.064	1.5	0.853	1.7	0.096	0.7	0.518	1.3	0.029	1.5	0.42	593	4	579	75	583	10	-2
8.1	0.08	35.7	153	425	0.4	0.063	0.8	0.850	0.9	0.098	0.4	0.114	1.4	0.030	1.5	0.45	601	2	663	26	585	11	10
9.1	-0.09	14.3	61	170	0.4	0.062	1.3	0.837	1.4	0.098	0.6	0.114	2.2	0.030	2.4	0.44	603	4	686	33	609	16	14
10.1 ^(*)	-0.08	8.8	181	111	1.7	0.065	1.7	0.836	1.8	0.093	0.8	0.517	1.4	0.028	1.7	0.42	573	4	684	37	567	9	19
11.1 ^(*)	0.99	19.6	183	256	0.7	0.058	2.4	0.708	2.4	0.088	0.6	0.249	1.7	0.030	1.8	0.23	544	3	573	90	548	17	5

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3.1(*)	1.45	11.8	90	144	0.64	0.063	5.9	0.82	6.2	0.094	1.6	0.260	3.9	0.034	5.5	0.26	579	9	710	126	673	38	23																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	

Shrimp data

4.1	0.02	49.2	252	573	0.5	0.060	0.8	0.825	0.9	0.100	0.4	0.142	1.5	0.031	1.6	0.43	614	2	598	17	617	10	-3
5.1	0.53	54.5	268	645	0.4	0.059	3.2	0.799	3.2	0.098	0.4	0.138	2.7	0.029	3.9	0.12	601	2	577	70	578	23	-4

(*) Results not used in age calculations.

Table 3

LA-ICPMS

Sample	Pb total	Pb rad	Th	U	Th/U	²⁰⁷ Pb/ ²³⁵ U	1 σ	²⁰⁶ Pb/ ²³⁸ U	1 σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb	1 σ	²⁰⁸ Pb/ ²⁰⁶ Pb	1 σ	²⁰⁶ Pb/ ²³⁸ U	1 σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1 σ	Concord.
spot	(common)	ppm	ppm	ppm															(%)
SR-07 São Roque Granite																			
										UTM S: 7405597 x 284394, 23K									
										concordia age: 604.2±3.2 Ma									
										Age (Ma)									
1.1 ^(*)	2.0	54.8	580	417	1.4	1.218	0.143	0.118	0.003	0.80	0.075	0.010	0.218	0.073	720	17	1061	214	67
2.1	0.6	108	600	961	0.6	0.816	0.039	0.098	0.001	0.37	0.060	0.003	0.164	0.047	604	8	613	108	98
3.1	3.7	103	602	823	0.7	0.830	0.052	0.100	0.002	0.51	0.060	0.004	0.221	0.033	615	10	610	141	100
4.1	0.8	62.7	372	562	0.7	0.762	0.052	0.095	0.002	0.50	0.058	0.004	0.220	0.016	587	9	527	143	111
4.2	0.1	83.6	560	695	0.8	0.806	0.048	0.096	0.002	0.20	0.061	0.004	0.286	0.015	591	9	635	133	93
5.1	0.5	95.8	830	769	1.1	0.780	0.045	0.097	0.002	0.01	0.059	0.004	0.305	0.022	594	9	555	129	107
6.1	0.8	92.5	738	794	0.9	0.773	0.042	0.095	0.001	0.64	0.059	0.003	0.242	0.028	583	8	575	120	101
7.1	1.0	82.6	488	762	0.6	0.802	0.038	0.098	0.001	0.68	0.060	0.003	0.099	0.043	601	8	587	106	102
7.2	0.4	113	926	929	1.0	0.782	0.050	0.094	0.002	0.81	0.060	0.004	0.277	0.045	579	9	616	143	94
8.1	0.6	86.3	512	777	0.7	0.815	0.045	0.098	0.002	0.46	0.060	0.003	0.227	0.014	601	9	619	124	97
9.1	0.1	93.4	595	813	0.7	0.825	0.044	0.100	0.002	0.70	0.060	0.003	0.252	0.010	611	9	608	117	100
10.1	0.2	96.0	672	815	0.8	0.840	0.041	0.099	0.001	0.71	0.061	0.003	0.266	0.009	611	8	649	113	94
11.1	0.0	81.9	493	711	0.7	0.837	0.048	0.099	0.002	0.86	0.061	0.004	0.220	0.024	609	9	649	130	93
12.1	0.9	112	760	977	0.8	0.799	0.041	0.098	0.001	0.70	0.059	0.003	0.234	0.026	605	8	563	117	107
13.1	0.8	66.8	345	594	0.6	0.818	0.059	0.099	0.002	0.54	0.060	0.005	0.201	0.010	608	11	603	165	100
14.1	0.9	73.1	435	628	0.7	0.784	0.047	0.098	0.002	0.28	0.058	0.004	0.241	0.011	600	9	539	140	111
15.1	0.2	100	639	843	0.8	0.818	0.044	0.097	0.002	0.46	0.061	0.003	0.299	0.019	599	9	636	121	94
16.1	0.4	127	921	1039	0.9	0.797	0.042	0.097	0.002	0.18	0.060	0.003	0.268	0.028	595	9	595	118	100
17.1	0.5	73.3	451	633	0.7	0.810	0.050	0.100	0.002	0.07	0.059	0.004	0.242	0.008	613	10	562	134	109
18.1 ^(*)	0.0	44.5	2.7	142	0.0	5.780	0.175	0.323	0.004	0.88	0.130	0.004	0.029	0.003	1806	19	2093	42	86
18.2 ^(*)	2.6	68.7	737	595	1.2	0.821	0.079	0.101	0.002	0.45	0.059	0.006	0.231	0.017	622	13	559	198	111
19.1	0.4	84.1	464	716	0.6	0.807	0.050	0.099	0.002	0.39	0.059	0.004	0.217	0.012	609	10	572	146	106
20.1	0.0	108	733	922	0.8	0.825	0.045	0.098	0.002	0.65	0.061	0.003	0.230	0.038	600	9	650	118	92
21.1 ^(*)	1.3	46.4	231	406	0.6	0.835	0.071	0.101	0.002	0.28	0.060	0.006	0.184	0.016	620	12	603	198	102
22.1	0.5	99.5	654	850	0.8	0.826	0.039	0.098	0.001	0.72	0.061	0.003	0.267	0.016	604	8	640	105	94
23.1	0.0	651	9245	3735	2.5	0.847	0.025	0.100	0.001	0.96	0.061	0.002	0.655	0.151	617	7	644	66	95
MD42B- Cantareira syenogranite																			
										UTM S: 7403145 x 321574; 23K									
										concordia age: 591.9±3.7 Ma									
1.1 ^(*)	2.2	35.4	161	306	0.5	0.638	0.100	0.083	0.002	0.01	0.056	0.010	0.142	0.023	516	14	433	340	119
2.1	1.0	50.2	201	420	0.5	0.743	0.061	0.093	0.002	0.62	0.058	0.005	0.159	0.036	571	10	534	189	106
3.1	0.5	98.0	585	808	0.7	0.767	0.044	0.094	0.001	0.01	0.059	0.004	0.203	0.018	579	8	575	135	100

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LA-ICPMS

4.1	0.4	69.1	349	576	0.6	0.751	0.071	0.093	0.002	0.28	0.058	0.006	0.154	0.050	576	11	541	227	106
5.1(*)	0.5	53.0	367	409	0.9	0.814	0.072	0.094	0.002	0.01	0.063	0.006	0.223	0.076	580	11	700	224	82
6.1(*)	1.6	40.9	249	333	0.8	0.747	0.105	0.094	0.003	0.01	0.057	0.009	0.236	0.020	581	14	506	314	114
7.1(*)	14.3	325	542	759	0.7	7.279	0.194	0.343	0.003	0.84	0.154	0.004	0.177	0.013	1903	16	2388	47	79
8.1(*)	3.4	30.4	105	279	0.4	0.767	0.075	0.095	0.002	0.26	0.058	0.006	0.128	0.034	588	11	541	237	108
8.2	0.9	81.2	335	691	0.5	0.766	0.049	0.096	0.001	0.58	0.058	0.004	0.147	0.011	590	8	528	147	111
9.1	0.0	74.1	400	618	0.6	0.749	0.058	0.094	0.002	0.51	0.058	0.005	0.178	0.017	578	9	528	181	109
10.1	0.4	71.6	352	587	0.6	0.773	0.055	0.096	0.002	0.25	0.058	0.005	0.169	0.020	593	9	536	171	110
11.1	0.0	50.7	145	458	0.3	0.757	0.062	0.094	0.002	0.29	0.059	0.005	0.105	0.010	577	10	553	186	104
12.1	0.6	75.9	429	615	0.7	0.804	0.050	0.097	0.001	0.13	0.060	0.004	0.253	0.037	595	8	617	141	96
13.1	0.1	87.0	396	745	0.5	0.787	0.039	0.095	0.001	0.01	0.060	0.003	0.141	0.025	587	7	600	120	97
14.1	0.3	76.2	407	645	0.6	0.798	0.041	0.097	0.001	0.17	0.060	0.003	0.152	0.033	597	7	588	124	101
15.1	0.4	72.3	332	602	0.6	0.813	0.040	0.100	0.001	0.64	0.059	0.003	0.205	0.014	612	7	575	109	106
16.1	1.9	67.5	298	566	0.5	0.804	0.041	0.099	0.001	0.37	0.059	0.003	0.187	0.009	609	7	562	118	108
17.1(*)	0.3	45.0	233	355	0.7	0.846	0.056	0.102	0.002	0.17	0.060	0.004	0.186	0.032	626	9	608	160	103
18.1	0.4	51.7	181	452	0.4	0.809	0.044	0.098	0.001	0.51	0.060	0.004	0.127	0.014	600	8	608	128	98
19.1	0.1	56.7	197	494	0.4	0.816	0.045	0.097	0.001	0.04	0.061	0.004	0.144	0.010	597	8	641	132	93
20.1	1.0	54.0	280	459	0.6	0.775	0.046	0.095	0.001	0.31	0.059	0.004	0.206	0.010	585	8	574	132	101
21.1	1.0	54.9	238	478	0.5	0.781	0.045	0.096	0.001	0.29	0.059	0.004	0.173	0.009	591	8	564	131	104
22.1	0.5	42.7	204	364	0.6	0.790	0.055	0.094	0.002	0.16	0.061	0.005	0.180	0.023	578	9	643	162	89
23.1	0.0	70.1	376	570	0.7	0.791	0.046	0.095	0.001	0.13	0.060	0.004	0.219	0.021	586	8	616	144	95
24.1	0.1	91.6	326	780	0.4	0.809	0.036	0.098	0.001	0.27	0.060	0.003	0.131	0.009	601	7	605	107	99
25.1(*)	0.8	28.7	116	252	0.5	0.809	0.078	0.096	0.002	0.01	0.061	0.007	0.172	0.016	590	11	649	230	90
MD24- Fazenda Itahyê Granite																			concordia age: 598.3±3.5 Ma
1.1	0.4	52.5	368	409	0.9	0.824	0.056	0.097	0.002	0.01	0.062	0.004	0.274	0.030	595	10	665	156	
2.1	0.4	56.9	346	462	0.7	0.844	0.051	0.096	0.002	0.17	0.064	0.004	0.218	0.048	593	10	726	139	81
3.1	0.4	50.3	293	390	0.8	0.818	0.054	0.098	0.002	0.01	0.061	0.004	0.282	0.017	603	10	623	153	96
4.1	0.6	54.6	258	468	0.6	0.825	0.053	0.097	0.002	0.41	0.062	0.004	0.189	0.010	594	10	673	148	88
5.1	0.7	55.4	355	449	0.8	0.805	0.048	0.094	0.002	0.13	0.062	0.004	0.261	0.023	582	9	667	153	87
6.1	0.1	59.8	399	466	0.9	0.769	0.044	0.095	0.002	0.44	0.059	0.004	0.327	0.013	585	9	558	134	104
7.1	0.4	42.0	285	337	0.8	0.834	0.069	0.097	0.002	0.01	0.063	0.006	0.229	0.029	596	12	690	196	86
8.1	0.3	76.1	522	593	0.9	0.826	0.043	0.096	0.001	0.56	0.063	0.003	0.328	0.020	591	8	690	117	85
9.1	0.3	60.7	343	494	0.7	0.795	0.046	0.094	0.002	0.10	0.062	0.004	0.231	0.021	576	9	662	133	86
10.1(*)	0.1	169.4	47	228	0.2	22.983	0.573	0.613	0.006	0.64	0.272	0.006	0.049	0.003	3083	24	3316	36	92
10.2	0.4	45.4	286	359	0.8	0.755	0.058	0.095	0.002	0.65	0.058	0.005	0.287	0.023	583	11	524	165	111

UTM S: 7406817 x 314682, 23K

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LA-ICPMS

11.1	0.5	46.9	326	371	0.9	0.833	0.058	0.097	0.002	0.44	0.062	0.005	0.250	0.034	597	11	681	170	87
12.1(*)	0.8	32.2	219	262	0.8	0.778	0.070	0.101	0.002	0.01	0.056	0.006	0.216	0.013	617	13	459	217	134
13.1	0.2	77.1	471	590	0.8	0.784	0.029	0.095	0.001	0.79	0.060	0.003	0.227	0.032	587	6	591	91	99
14.1	0.7	38.6	232	323	0.7	0.794	0.045	0.099	0.002	0.19	0.058	0.004	0.210	0.014	607	9	540	137	112
15.1	0.3	56.5	420	441	1.0	0.821	0.036	0.101	0.001	0.01	0.059	0.003	0.311	0.008	619	8	570	99	108
16.1	1.2	46.2	268	390	0.7	0.791	0.044	0.098	0.002	0.39	0.058	0.004	0.203	0.020	605	9	542	132	111
17.1	0.5	61.3	416	487	0.9	0.808	0.035	0.099	0.001	0.52	0.059	0.003	0.306	0.011	610	8	568	96	107
18.1	0.5	47.7	317	398	0.8	0.780	0.036	0.096	0.001	0.69	0.059	0.003	0.263	0.016	591	8	563	105	105
19.1	1.4	51.0	349	416	0.8	0.814	0.041	0.101	0.002	0.68	0.058	0.003	0.251	0.012	622	9	540	116	115
20.1	1.0	27.7	241	215	1.1	0.853	0.060	0.101	0.002	0.12	0.061	0.005	0.218	0.020	620	12	648	165	95
21.1	1.0	52.1	348	418	0.8	0.815	0.034	0.098	0.001	0.30	0.060	0.003	0.263	0.060	605	7	606	98	99
22.1	0.9	52.6	380	424	0.9	0.816	0.038	0.098	0.001	0.41	0.060	0.003	0.295	0.010	603	8	614	109	98
23.1	0.6	28.4	122	252	0.5	0.807	0.058	0.095	0.002	0.24	0.062	0.005	0.161	0.017	586	11	659	181	88
24.1	1.4	30.7	173	267	0.6	0.842	0.045	0.099	0.002	0.01	0.062	0.004	0.184	0.012	606	9	673	137	90
25.1	0.5	69.0	467	566	0.8	0.781	0.029	0.095	0.001	0.01	0.060	0.002	0.286	0.008	584	7	591	81	98

JP-18 Vila dos Remédios Quartz Syenite

UTM S: 7424373 x 337585, 23K

concordia age: 591.2 ±3.4 Ma

1.1N						0.799	0.016	0.097	0.001	0.63	0.060	0.001	0.139	1.305	597	7	599	31	100
1.2B						0.768	0.018	0.095	0.001	0.52	0.059	0.001	0.082	0.691	583	7	578	40	101
2.1						0.718	0.024	0.082	0.001	0.49	0.064	0.002	0.172	1.308	511	8	722	52	71
3.1(*)																			
4.1						0.783	0.015	0.097	0.001	0.68	0.060	0.001	0.225	1.437	594	7	592	34	100
5.1						0.766	0.017	0.094	0.001	0.55	0.060	0.001	0.179	1.060	580	7	600	39	97
6.1						0.806	0.025	0.095	0.001	0.40	0.059	0.002	0.217	1.204	584	7	577	55	101
7.1						0.775	0.032	0.094	0.002	0.44	0.060	0.002	0.233	1.199	581	10	601	75	97
8.1(*)						0.838	0.018	0.103	0.001	0.60	0.061	0.001	0.329	1.589	631	8	634	40	100
9.1(*)						0.876	0.019	0.102	0.001	0.62	0.061	0.001	0.265	1.206	627	8	628	44	100
10.1						0.786	0.016	0.097	0.001	0.62	0.060	0.001	0.219	0.947	594	7	605	31	98
11.1(*)						0.697	0.017	0.088	0.001	0.57	0.059	0.001	0.327	1.338	542	7	548	42	99
12.1						0.818	0.016	0.099	0.001	0.61	0.060	0.001	0.389	1.515	607	7	582	32	104
13.1(*)						0.858	0.023	0.103	0.001	0.43	0.061	0.001	0.975	0.354	630	7	633	45	100
14.1(*)						0.882	0.022	0.104	0.002	0.65	0.061	0.002	0.600	0.225	636	10	645	55	99
15.1(*)						0.752	0.016	0.092	0.001	0.51	0.059	0.001	0.614	0.235	566	6	568	31	100
16.1						0.772	0.016	0.098	0.001	0.66	0.060	0.001	0.609	0.241	604	8	603	45	100
17.1						0.785	0.019	0.096	0.001	0.59	0.060	0.001	0.516	0.210	593	8	594	42	100
18.1						0.788	0.010	0.097	0.001	0.70	0.060	0.001	0.477	0.198	596	5	594	23	100
19.1						0.775	0.009	0.094	0.001	0.69	0.060	0.001	0.304	0.130	582	5	582	18	100

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LA-ICPMS

20.1(*)	0.815	0.011	0.099	0.001	0.75	0.060	0.001	0.482	0.212	610	6	612	19	100
21.1	0.795	0.018	0.097	0.001	0.44	0.060	0.001	0.492	0.224	596	6	589	41	101
22.1(*)	0.824	0.016	0.100	0.001	0.67	0.061	0.001	0.352	0.169	615	8	617	49	100
23.1(*)	0.771	0.012	0.093	0.001	0.62	0.060	0.001	0.403	0.196	572	5	586	28	98
24.1(*)	0.649	0.020	0.082	0.001	0.44	0.058	0.001	0.289	0.146	510	6	508	47	100
25.1	0.807	0.011	0.097	0.001	0.64	0.060	0.001	0.413	0.215	596	5	597	25	100

Table 4

Table 4. Results of LA-ICPMS in situ Hf isotope determinations in zircon crystals from SRD granites.

Spot #	Age	176Hf/177Hf	2se	176Lu/177Hf	2se	176Hf/177Hf	ϵ Hf(0)	ϵ Hf(t)	Hf T(DM)			
1	(t, Ma)		*10e6		*10e6	(t)			interm.	felsic	wr	zr
SR-07 São Roque Granite				UTM S: 7405597 x 284394, 23K								
61	603	0.281720	36	0.00073	22	0.281711	-37.2	-24.3	3015	2551	2294	2114
451	603	0.281733	29	0.00047	12	0.281728	-36.7	-23.7	2979	2521	2268	2081
561	603	0.281805	23	0.00060	8	0.281798	-34.2	-21.2	2825	2397	2160	1989
371	603	0.281720	26	0.00047	10	0.281714	-37.2	-24.2	3009	2546	2290	2100
281	603	0.281729	25	0.00059	15	0.281723	-36.9	-23.9	2990	2531	2277	2093
23.1	603	0.281828	46	0.00277	212	0.281797	-33.4	-21.2	2827	2398	2161	2074
110.1	603	0.281751	64	0.00074	19	0.281743	-36.1	-23.1	2946	2495	2245	2071
18.1	2093	0.281114	22	0.00114	24	0.281069	-58.6	-13.5	3497	3225	3075	2979
17.1	603	0.281760	22	0.00061	6	0.281753	-35.8	-22.8	2923	2476	2229	2051
21.1	603	0.281799	31	0.00039	3	0.281795	-34.4	-21.3	2832	2403	2165	1986
20.1	603	0.281761	20	0.00049	17	0.281756	-35.7	-22.7	2917	2472	2225	2043
average		0.281761	32	0.00079	32	0.281752	-35.8	-22.8	2926	2479	2231	2060
1σsigma		0.000038		0.00071		0.000034	1.4	1.2	75	61	53	44
ITQ-2 Itaqui Granite				UTM S: 7401288 x 306170; 23K								
91	594	0.281867	27	0.00072	5	0.281859	-32.0	-19.2	2697	2291	2054	1909
631	594	0.281887	23	0.00074	8	0.281879	-31.3	-18.5	2652	2255	2023	1882
14.1	594	0.281948	22	0.00051	4	0.281942	-29.2	-16.3	2513	2143	1926	1787
12.1	594	0.281947	26	0.00101	11	0.281935	-29.2	-16.5	2528	2154	1936	1812
13.1	594	0.281889	25	0.00070	13	0.281881	-31.2	-18.4	2647	2251	2019	1877
10.1	594	0.281934	24	0.00108	10	0.281922	-29.6	-17.0	2556	2178	1956	1833
4.1	594	0.281905	22	0.00056	24	0.281899	-30.7	-17.8	2608	2219	1992	1848
3.1	594	0.281868	29	0.00102	29	0.281856	-32.0	-19.3	2702	2296	2058	1923
2.1	594	0.281919	25	0.00084	10	0.281910	-30.2	-17.4	2584	2200	1976	1843
3.1	594	0.281973	24	0.00072	16	0.281965	-28.3	-15.5	2462	2102	1891	1762
14.1	594	0.281977	29	0.00109	49	0.281965	-28.1	-15.5	2462	2101	1891	1773
average		0.281919	25	0.00082	16	0.281910	-30.2	-17.4	2583	2199	1975	1841
1σsigma		0.000039		0.00020		0.000039	1.4	1.4	86	70	60	54
ITQ - E Itaqui Granite mafic enclave				UTM S: 7401288 x 306170; 23K								
11	594	0.281942	51	0.00072	15	0.281934	-29.4	-16.6	2532	2158	2077	1806
211	594	0.281982	48	0.00099	14	0.281971	-27.9	-15.2	2448	2090	2013	1761
32.1	594	0.281899	39	0.00067	4	0.281892	-30.9	-18.1	2624	2232	2148	1862
11.1	594	0.282111	77	0.00377	19	0.282069	-23.4	-11.8	2232	1915	1847	1706
4.1	594	0.281910	38	0.00075	2	0.281902	-30.5	-17.7	2602	2215	2131	1851
561	594	0.281822	39	0.00098	6	0.281811	-33.6	-20.9	2802	2376	2285	1985
6.1	594	0.281850	44	0.00096	4	0.281840	-32.6	-19.9	2739	2325	2236	1944
7.1	594	0.281789	39	0.00075	12	0.281781	-34.7	-22.0	2867	2429	2335	2018
8.1	594	0.281983	55	0.00073	11	0.281975	-27.9	-15.1	2441	2084	2007	1749
9.1	594	0.281943	50	0.00032	3	0.281939	-29.3	-16.4	2519	2148	2068	1785
10.1	594	0.282138	88	0.00347	26	0.282099	-22.4	-10.7	2165	1861	1796	1651
average		0.281902	45	0.00076	8	0.281894	-30.8	-18.0	2619	2229	2145	1862
1σsigma		0.000069	6	0.000207	5	0.000070	2.4	2.5	153	124	118	99
MD-24 Faz. Itahyê Granite				UTM S: 7406817 x 314682, 23K								
11	598	0.281872	34	0.00033	3	0.281868	-31.8	-18.8	2673	2273	2023	1883
291	598	0.281998	26	0.00074	22	0.281990	-27.4	-14.5	2404	2055	1837	1728
40.1	598	0.281911	28	0.00059	5	0.281905	-30.4	-17.5	2593	2208	1967	1841
5.1	598	0.281925	27	0.00040	2	0.281920	-30.0	-17.0	2558	2180	1943	1814

9.1	598	0.281982	21	0.00078	5	0.281974	-27.9	-15.1	2440	2085	1862	1751
24.1	598	0.281876	23	0.00045	5	0.281871	-31.7	-18.7	2668	2269	2019	1884
28.1	598	0.281952	27	0.00057	6	0.281945	-29.0	-16.1	2503	2135	1905	1784
25.1	598	0.281925	28	0.00053	4	0.281919	-30.0	-17.0	2562	2183	1945	1820
21.1	598	0.281896	26	0.00058	4	0.281890	-31.0	-18.0	2626	2235	1990	1862
22.1	598	0.281945	31	0.00065	8	0.281938	-29.2	-16.3	2519	2148	1916	1797
10.1*	598	0.281539	37	0.00055	6	0.281533	-43.6	-30.7	3407	2868	2530	2352
average		0.281928	27	0.00056	6	0.281922	-29.8	-16.9	2555	2177	1941	1816
1 sigma		0.000042		0.00014		0.000041	1.5	1.4	90	73	62	53
MD-42B Cantareira Syenogranite UTM S: 7403145 x 321574; 23K												
9.1	592	0.282140	24	0.00036	3	0.282136	-22.3	-9.5	2084	1795	1551	1515
10.1	592	0.282068	24	0.00046	8	0.282063	-24.9	-12.1	2247	1927	1656	1619
11.1	592	0.282105	28	0.00024	3	0.282103	-23.6	-10.6	2158	1855	1599	1558
13.1	592	0.282103	20	0.00036	3	0.282099	-23.7	-10.8	2166	1862	1604	1566
12.1	592	0.282093	31	0.00045	14	0.282088	-24.0	-11.1	2190	1881	1619	1583
14.1	592	0.282092	20	0.00030	11	0.282088	-24.1	-11.1	2190	1881	1619	1579
15.1	592	0.282125	21	0.00024	3	0.282122	-22.9	-9.9	2115	1820	1571	1531
16.1	592	0.282064	25	0.00036	5	0.282060	-25.0	-12.1	2252	1931	1659	1619
20.1	592	0.282108	20	0.00028	6	0.282105	-23.5	-10.5	2152	1850	1595	1555
22.1	592	0.282111	26	0.00036	4	0.282107	-23.4	-10.5	2149	1847	1593	1555
23.1	592	0.282117	25	0.00032	4	0.282114	-23.2	-10.2	2134	1835	1583	1545
16.3	592	0.282005	26	0.00040	14	0.282001	-27.1	-14.2	2385	2038	1821	1703
average		0.282094	24	0.00035	7	0.282090	-24.0	-11.1	2185	1877	1622	1577
1 sigma		0.000035		0.00007		0.000036	1.3	1.3	79	64	70	50
CANT-6 Cantareira Monzogranite UTM S: 7409165 x 323786; 23K												
1.1	598	0.281984	16	0.00036	4	0.281980	-27.8	-14.8	2425	2072	1780	1729
2.1	598	0.281965	25	0.00033	5	0.281961	-28.5	-15.5	2468	2107	1808	1755
3.1	598	0.281949	21	0.00030	3	0.281945	-29.1	-16.1	2503	2135	1830	1776
4.1	598	0.281926	22	0.00038	2	0.281921	-29.9	-16.9	2556	2178	1865	1812
7.1	598	0.281994	24	0.00086	30	0.281984	-27.5	-14.7	2417	2066	1774	1739
5.1	598	0.281927	23	0.00055	13	0.281921	-29.9	-16.9	2558	2179	1866	1818
12.1	598	0.281907	21	0.00047	7	0.281902	-30.6	-17.6	2599	2213	1893	1841
6.1	598	0.281930	21	0.00054	11	0.281924	-29.8	-16.8	2551	2174	1862	1813
8.1	598	0.281934	23	0.00064	6	0.281927	-29.6	-16.7	2543	2168	1857	1812
9.1	598	0.281875	23	0.00044	11	0.281870	-31.7	-18.7	2669	2269	1938	1884
10.1	598	0.281856	31	0.00168	20	0.281837	-32.4	-19.9	2741	2328	1986	1973
average		0.281932	23	0.00060	10	0.281925	-29.7	-16.8	2548	2172	1860	1814
1 sigma		0.000042		0.00039		0.000044	1.5	1.6	98	79	64	70
TAP-1 Taipas Granite UTM S: 7406490 x 323475; 23K												
1.1	598	0.282096	28	0.00043	20	0.282091	-23.9	-10.9	2181	1874	1632	1579
2.1	598	0.282111	24	0.00071	33	0.282103	-23.4	-10.5	2153	1852	1614	1569
4.1	598	0.282104	23	0.00050	7	0.282099	-23.6	-10.6	2164	1860	1621	1570
5.1	598	0.282095	27	0.00055	21	0.282089	-23.9	-11.0	2184	1877	1635	1584
6.1	598	0.282047	26	0.00053	15	0.282041	-25.6	-12.7	2290	1963	1704	1650
7.1	598	0.282082	18	0.00045	4	0.282077	-24.4	-11.4	2212	1900	1653	1599
7.2	598	0.282046	25	0.00092	18	0.282036	-25.7	-12.9	2303	1973	1712	1669
8.1	598	0.282012	20	0.00053	6	0.282006	-26.9	-13.9	2368	2026	1755	1699
13.1	598	0.282027	26	0.00045	14	0.282022	-26.3	-13.4	2333	1998	1732	1675
14.1	598	0.281605	25	0.00037	5	0.281600	-41.3	-28.3	3260	2749	2343	2251
9.1	598	0.282061	20	0.00044	5	0.282056	-25.2	-12.2	2259	1938	1683	1628

average		0.282068	24	0.00055	14	0.282062	-24.9	-11.9	2245	1926	1674	1622
1 sigma		0.000034	3	0.00015	9	0.000034	1.2	1.2	76	62	50	48
PE-04 Perus Granite		UTM S: 7409208 x 322911; 23K										
1-1	598	0.281920	53	0.00529	44	0.281861	-30.1	-19.1	2689	2286	2084	-8278
2-1	598	0.281978	42	0.00432	13	0.281930	-28.1	-16.6	2538	2163	1937	-7572
3-1	598	0.281892	47	0.00494	63	0.281837	-31.1	-19.9	2743	2329	2107	-8531
3-2	598	0.281915	46	0.00459	63	0.281864	-30.3	-19.0	2683	2281	2050	-8249
4-1	598	0.281923	47	0.00432	9	0.281875	-30.0	-18.6	2659	2262	2022	-8138
5-1	598	0.281892	56	0.00435	25	0.281843	-31.1	-19.7	2728	2318	2071	-8464
6-1	598	0.281952	57	0.00512	74	0.281894	-29.0	-17.9	2616	2226	2025	-7934
7-1	598	0.281874	51	0.00434	36	0.281826	-31.7	-20.3	2767	2349	2098	-8647
8-1	598	0.282017	62	0.00557	93	0.281955	-26.7	-15.7	2482	2118	1948	-7315
9-1	598	0.281975	109	0.01033	47	0.281859	-28.2	-19.1	2694	2290	2351	-8302
10-1	598	0.281953	42	0.00417	11	0.281906	-29.0	-17.5	2590	2206	1968	-7816
average		0.281936	56	0.00521	43	0.281877	-29.6	-18.5	2653	2257	2060	
1 sigma		0.000043		0.00176		0.000040	1.5	1.4	89	72	113	
TICO-2 Tico-Tico Granite		UTM S: 7413075 x 318718, 23 K										
10-1	591	0.282087	23	0.00111	37	0.282075	-24.2	-11.7	2221	1906	2033	1620
11-1	591	0.282096	24	0.00088	35	0.282086	-23.9	-11.2	2195	1885	2010	1597
12-1	591	0.282103	19	0.00071	5	0.282095	-23.7	-10.9	2176	1870	1993	1581
13-1	591	0.282106	26	0.00062	3	0.282099	-23.6	-10.8	2167	1862	1985	1572
14-1	591	0.282073	19	0.00066	6	0.282065	-24.7	-12.0	2242	1922	2051	1620
15-1	591	0.282088	21	0.00077	7	0.282079	-24.2	-11.5	2211	1897	2024	1604
16-1	591	0.282071	25	0.00086	19	0.282062	-24.8	-12.1	2250	1929	2058	1631
17-2	591	0.282078	20	0.00101	13	0.282067	-24.6	-11.9	2239	1920	2049	1628
18-1	1839	0.281803	25	0.00072	2	0.281780	-34.3	3.7	2137	2059	2090	1986
19-1	2117	0.281654	24	0.00067	4	0.281628	-39.5	6.9	2219	2199	2207	2181
20-1	591	0.282090	26	0.00075	9	0.282081	-24.1	-11.4	2206	1894	2020	1600
average		0.282088	23	0.00082	15	0.282079	-24.2	-11.5	2212	1898	2025	1606
1 sigma		0.000012		0.00016		0.000013	0.4	0.5	29	24	26	21

37 analyses in gray not used in the average calculation
 38 Hf model ages (Hf T(DM) calculated for different 176Lu/177Hf: intermediate crust (0.015); felsic crust (0.093);
 39 w (from whole-rock IPCMS results); zrn (from zircon results, column E)
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Table 1

(%)	SR-07	SR-05	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Cant-6	MD-42B	TAP-01	TAD-01	TICO-1	TICO-2	Pe-04
SiO ₂	64.46	75.80	67.61	65.81	51.18	73.49	64.68	68.54	72.28	68.47	74.59	73.55	73.97	74.30
TiO ₂	0.864	0.114	0.787	0.759	1.627	0.04	0.882	0.581	0.449	0.601	0.027	0.13	0.123	0.077
Al ₂ O ₃	14.49	12.74	13.33	14.72	15.87	14.32	14.96	14.73	13.63	15.18	13.55	13.75	13.83	14.44
Fe ₂ O _{3(t)}	5.07	1.35	4.85	4.67	10.40	0.18	4.99	3.13	1.99	2.84	0.45	1.82	1.59	1.23
MnO	0.080	0.053	0.081	0.080	0.197	0.00	0.092	0.065	0.039	0.049	0.012	0.088	0.076	0.029
MgO	1.72	0.17	1.85	1.65	4.52	<0,01	1.70	0.69	0.50	0.80	<0,01	0.06	0.05	0.06
CaO	3.27	1.19	3.79	3.65	7.42	0.84	3.45	2.13	1.91	2.51	0.79	0.66	1.02	0.77
Na ₂ O	3.04	3.40	3.47	3.51	3.93	4.59	3.38	3.72	3.84	3.88	3.32	3.23	3.08	3.81
K ₂ O	4.79	4.44	2.91	4.13	3.04	4.88	4.26	5.02	4.07	4.30	6.14	5.16	4.81	3.91
P ₂ O ₅	0.318	0.045	0.347	0.284	0.676	0.05	0.379	0.199	0.141	0.207	0.000	0.115	0.099	0.070
LOI	1.88	0.73	0.60	0.57	0.85	0.82	0.92	0.80	0.68	0.57	0.31	0.70	0.75	0.47
SUM	99.98	100.03	99.63	99.83	99.71	99.19	99.69	99.60	99.53	99.41	99.19	99.27	99.39	99.17
(ppm)														
Ba (MS)	1415	342	635	1189	580	52.6	1467	1481	802	1222	58.2	65.7	75.2	16.7
Ce	120	37.2	103	112	118	17.0	106	72	58.0	78.6	3.41	33.0	30.9	53.1
Co	10	<6	11	9	27	<6	9	5	<6	6	<6	<6	<6	<6
Cr	20	<13	37	35	22	<13	17	22	<13	<13	<13	15	18	<13
Cs	1.80	2.51	2.08	2.30	2.59	6.19	1.13	2.01	2.26	8.15	2.29	3.10	4.19	6.61
Cu	9	<5	7	15	117	<5	9	7	<5	<5	<5	<5	<5	<5
Dy	3.87	1.91	2.84	2.72	4.75	3.56	3.80	1.45	1.41	1.90	0.06	5.89	4.27	7.35
Er	1.72	1.03	1.23	1.20	2.14	1.70	1.75	0.53	0.49	0.78	0.04	2.86	2.19	3.83
Eu	2.01	0.57	1.79	1.75	2.96	0.23	2.06	1.22	1.05	1.45	0.07	0.25	0.28	0.16
F	746	<500	1051	1042	1739	<500	775	1436	623	1283	<500	1561	2111	<500
Ga	20	16	18	18	24	21	18	22	20	21	24	23	21	20
Gd	6.73	2.77	4.70	4.61	7.78	3.34	6.60	2.97	2.97	3.36	0.09	3.89	3.16	6.63
Hf	6.18	3.33	5.42	5.31	5.37	1.80	6.27	4.29	4.71	5.99	2.23	2.89	3.27	1.72

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Table 1

(ppm)	SR-07	SR-05	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Cant-6	MD-42B	TAP-01	TAD-01	TICO-1	TICO-2	Pe-04
Ho	0.67	0.36	0.53	0.51	0.90	0.69	0.67	0.25	0.20	0.35	0.01	1.20	0.88	1.45
La	60.0	17.9	52.6	59.9	50.0	8.09	53.3	41.2	29.0	39.6	2.04	16.5	15.8	23.2
Lu	0.21	0.16	0.17	0.17	0.30	0.22	0.18	0.06	0.06	0.10	0.02	0.31	0.28	0.55
Mo	n.a	n.a	1.37	0.86	0.75	0.19	n.a	1.46	n.a	1.63	<0.01	2.25	2.01	<0.01
Nb	22.6	14.5	15.2	16.9	20.7	23.2	17.4	8.66	9.91	10.3	0.45	18.0	25.4	4.0
Nd	48.4	15.5	40.8	40.1	55.0	7.36	44.7	29.4	22.8	29.9	1.05	13.3	12.3	20.3
Ni	11	< 5	12	13	11	< 5	9	< 5	< 5	5	< 5	< 5	< 5	< 5
Pb	26.1	33.0	18.4	23.0	17.5	78.6	23.1	25.9	35.6	29.1	66.0	24.6	27.8	49.0
Pr	13.2	4.23	11.3	11.3	14.1	1.97	11.9	7.96	6.32	8.28	0.32	3.85	3.56	5.69
Rb	133	157	100	118	117	242	115	140	138	141	170	217	255	245
S	<550	<550	< 550	< 550	1022	< 550	< 550	< 550	< 550	< 550	< 550	< 550	< 550	< 550
Sc	5.18	1.34	7.07	5.45	19.4	2.58	6.22	2.65	2.13	3.86	1.96	2.80	3.10	3.65
Sm	8.37	3.25	7.09	6.79	10.4	2.73	7.89	4.72	3.68	5.20	0.14	3.64	3.16	6.58
Sr (FRX)	713	184	763	861	795	59	810	670	426	641	92	34	35	28
Sr (MS)	754	202	818	913	811	68.6	858	664	465	695	93.9	31.7	34.2	30.5
Ta	n.a	n.a	1.08	1.03	1.20	3.14	n.a	0.47	n.a	0.65	0.08	1.95	2.42	0.87
Tb	0.78	0.37	0.59	0.57	0.97	0.64	0.77	0.34	0.32	0.41	0.01	0.92	0.68	1.30
Th	17	11	13	18	16	< 7	13	< 7	8	< 7	< 7	7	5	27
Th	14.8	12.3	10.8	13.0	8.22	5.22	10.9	10.1	8.12	8.6	11.4	8.67	7.61	14.1
Tm	0.23	0.15	0.18	0.18	0.31	0.25	0.23	0.07	0.06	0.11	0.01	0.41	0.33	0.61
U	7	7	< 3	< 3	3	15	5	< 3	5	< 3	3	7	6	< 3
U	3.20	6.34	2.50	3.01	1.93	19.1	2.75	2.51	2.81	1.57	6.35	5.18	5.32	8.15
V	85	< 9	82	73	231	< 9	72	41	35	49	9	5	6	< 9
W	n.a	n.a	0.28	0.26	0.30	1.27	n.a	0.17	n.a	0.65	0.39	3.31	2.30	0.83
Y	18.8	10.7	15.5	15.0	26.5	20.6	20.0	6.64	5.66	8.73	0.53	36.3	25.5	46.3
Yb	1.40	1.03	1.14	1.10	1.92	1.50	1.26	0.43	0.37	0.67	0.08	2.50	2.14	3.85
Zn	74	22	73	67	141	2	75	63	50	57	10	31	39	47
Zr	235	95	230	217	214	45	233	194	162	187	36	84	96	42

n.a = not analyzed

Table 1

	SR-07	SR-05	ITQ-02	ITQ-04	ITQ-E	ITQ-D1	MD-24	Cant-6	MD-42B	TAP-01	TAD-01	TICO-1	TICO-2	Pe-04
MgO/FeO(t)	0.38	0.14	0.43	0.40	0.48		0.38	0.25	0.28	0.31		0.04	0.03	0.05
Mg [#]	0.57	0.33	0.60	0.59	0.63		0.57	0.47	0.50	0.53		0.12	0.11	0.16
K ₂ O/Na ₂ O	1.6	1.3	0.9	1.2	0.8	1.1	1.3	1.3	1.1	1.1	1.8	1.6	1.6	1.1
Sr/Y	40	19	53	61	31	3.3	43	100	82	80	179	0.9	1.3	0.7
(La/Yb) _N	29	12	31	37	18	3.6	29	64	53	40	17	4.5	5.0	4.1
Eu _N /Eu*	0.82	0.58	0.95	0.95	1.01	0.23	0.87	0.99	0.97	1.06	1.83	0.21	0.27	0.08

PARTE V – DADOS SUPLEMENTARES

Tabela TS-1: Dados isotópicos U-Th-Pb para zircões do Granito Itaquera (amostra ITA-2), pertencente ao Domínio Embu, dos granitos Itu e Terra Nova (ITU-14X e TN-1), pertencentes ao Domínio Jundiaí, e do Charnockito Ubatuba (amostra CHA-1) do Domínio Costeiro.

Tabela TS-2: Dados de razões isotópicas Lu-Hf obtidos por LA-HR-ICPMS para as amostras de zircão dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e charnockito Ubatuba (CHA-1).

Figura FS-1: Diagramas de concórdia para granitos Itu (ITU-14X), Itaquera (ITA-2), Terra Nova (TN-1) e charnockito Ubatuba (CHA-1).

Figura FS-2: Imagens de catodoluminescência dos zircões analisados para as razões isotópicas U-Th-Pb e Lu-Hf, com os respectivos pontos amostrados em CHA-1 (charnockito Ubatuba), ITA-2 (Granito Itaquera), IA-10D (Ilha Anchieta), TN-1 (Granito Terra Nova), ITU-14X (Granito Itu).

Tabela TS-1: Dados isotópicos U-Th-Pb para zircões do Granito Itaquera (amostra ITA-2) pertencente ao Domínio Embu, dos granitos Itu e Terra Nova (ITU-14X e TN-1), pertencentes ao Domínio Jundiá, e do Charnockito Ubatuba (amostras CHA-1) do Domínio Costeiro.

Spot	%Pb _{total}	²⁰⁶ Pb _{red.}	Th	U	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	% err.	²⁰⁷ Pb/ ²³⁵ U	% err.	²⁰⁶ Pb/ ²³⁸ U	% err.	²⁰⁸ Pb/ ²⁰⁶ Pb	% err.	²⁰⁸ Pb/ ²³² Th	% err.	Rho	²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁸ Pb/ ²³² Th	1σ	% Discor dancia
	comum	(ppm)	(ppm)	(ppm)													idade		idade		idade		
CHA-1 - charnockito Ubatuba																	Idade concórdia = 582.4±2.4 Ma						
1.1	0.57	27.6	160	343	0.48	0.059	2.0	0.80	2.0	0.094	1.4	0.155	1.9	0.030	2.3	0.72	575	8	581	45	552	15	1
2.1	0.40	28.8	203	359	0.59	0.062	2.6	0.81	2.0	0.093	1.4	0.186	1.8	0.030	2.3	0.72	573	8	666	57	563	17	16
3.1	1.19	16.5	127	203	0.65	0.060	6.1	0.88	2.7	0.094	1.5	0.204	4.3	0.030	4.6	0.54	576	8	607	133	521	34	6
4.1	1.08	8.92	54	110	0.51	0.062	8.2	0.76	5.2	0.093	1.6	0.187	3.3	0.035	3.7	0.31	575	9	682	175	605	48	18
5.1	2.21	6.66	38	81	0.49	0.058	13.4	0.78	5.0	0.094	1.7	0.191	6.2	0.037	6.4	0.34	575	11	546	295	555	83	-5
6.1*	0.42	26.7	83	365	0.23	0.060	3.1	0.68	2.5	0.085	1.4	0.085	2.5	0.031	3.0	0.55	525	7	591	68	551	33	13
7.1	1.87	5.33	35	64	0.56	0.064	15.1	0.81	7.4	0.094	1.8	0.215	4.0	0.037	4.4	0.24	581	12	751	321	599	84	29
7.2	0.59	28.1	139	346	0.42	0.059	3.7	0.81	2.7	0.094	1.4	0.133	2.2	0.030	2.6	0.52	579	8	572	81	546	24	-1
8.1	0.17	13.1	117	158	0.76	0.065	4.1	0.84	2.6	0.096	1.5	0.243	2.4	0.031	2.9	0.59	590	9	783	87	599	23	33
9.1	1.08	17.5	130	215	0.62	0.066	5.3	0.78	5.1	0.093	1.5	0.226	3.1	0.034	3.4	0.29	576	8	793	111	610	28	38
10	1.10	33.9	282	413	0.71	0.060	4.7	0.82	3.5	0.095	1.4	0.234	2.0	0.032	2.5	0.40	582	8	610	103	567	20	5
11	0.56	15.3	98	181	0.56	0.064	3.1	0.87	2.9	0.098	1.5	0.184	2.7	0.032	3.1	0.52	600	9	754	66	599	22	26
12	1.67	22.0	138	264	0.54	0.062	6.8	0.82	4.5	0.095	1.4	0.198	2.1	0.036	2.5	0.32	587	8	664	147	581	36	13
13	0.36	14.7	111	176	0.65	0.062	5.9	0.74	4.5	0.096	1.5	0.225	2.8	0.034	3.2	0.33	596	9	689	126	643	32	16

* pontos não utilizados para determinação de idades.

Tabela TS-1: Dados isotópicos U-Th-Pb para zircões do Granito Itaquera (amostra ITA-2) pertencente ao Domínio Embu, dos granitos Itu e Terra Nova (ITU-14X e TN-1), pertencentes ao Domínio Jundiá, e do Charnockito Ubatuba (amostras CHA-1) do Domínio Costeiro.

Spot	%Pb _{total}	²⁰⁶ Pb _{red.}	Th	U	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	%	²⁰⁷ Pb/ ²³⁵ U	%	²⁰⁶ Pb/ ²³⁸ U	%	²⁰⁸ Pb/ ²⁰⁶ Pb	%	²⁰⁸ Pb/ ²³² Th	%		²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁸ Pb/ ²³² Th	1σ	%
	comum	(ppm)	(ppm)	(ppm)			err.		err.		err.		err.		err.	Rho	idade	idade	idade		Discor dancia		
ITA-1 - Granito Itaquera																	Idade concórdia = 593.5±2.2 Ma						
1.1	0.14	72.2	456	881	0.53	0.059	1.8	0.81	1.6	0.096	1.4	0.163	1.2	0.029	1.8	0.85	586.7	7.6	572	40	569	14	-3
2.1*	-0.03	299	1720	3454	0.51	0.059	0.6	0.86	1.5	0.101	1.3	0.153	1.5	0.030	2.5	0.90	618.8	7.9	583	12	599	12	-6
3.1	0.46	117	715	1397	0.53	0.059	2.4	0.84	1.6	0.097	1.4	0.165	0.9	0.030	1.7	0.91	596.8	8.2	576	51	570	16	-3
4.1	0.04	101	600	1233	0.50	0.061	2.1	0.82	1.5	0.095	1.3	0.153	1.1	0.029	1.8	0.88	585.0	7.6	643	45	572	16	10
5.1	0.12	150	861	1829	0.49	0.059	2.5	0.81	1.5	0.096	1.3	0.146	0.9	0.029	1.7	0.89	586.8	7.6	565	54	560	17	-4
6.1	0.11	175	1204	2108	0.59	0.060	1.3	0.85	1.6	0.097	1.3	0.175	0.7	0.029	1.6	0.85	592.5	7.6	590	29	561	11	0
7.1	-0.09	103	544	1229	0.46	0.061	0.9	0.84	1.6	0.098	1.4	0.137	1.1	0.029	1.8	0.87	600.8	7.8	640	20	590	11	7
8.1*	2.45	151	1790	1872	0.99	0.063	5.4	0.95	2.8	0.093	1.3	0.325	0.6	0.031	1.6	0.48	564.8	7.4	700	119	517	14	24
9.1	-0.02	120	886	1405	0.65	0.060	0.6	0.87	1.6	0.100	1.3	0.193	0.8	0.029	1.8	0.83	610.3	7.8	598	14	587	9	-2
10.1 [†]	3.51	143	1464	1946	0.78	0.062	7.3	0.94	2.7	0.084	1.5	0.263	2.5	0.029	3.2	0.53	509.1	7.3	672	160	411	22	32
11.1 [†]	5.43	15.7	141	545	0.27	0.063	14.0	0.04	136	0.030	1.5	0.315	2.2	0.040	3.0	0.01	200.9	3.4	722	299	505	50	260
12	0.24	78.9	555	940	0.61	0.059	1.5	0.84	1.6	0.098	1.4	0.186	1.1	0.030	1.9	0.86	599.5	7.8	579	34	578	12	-3
13	0.08	305	1996	3676	0.56	0.059	0.6	0.84	1.5	0.097	1.3	0.166	0.8	0.029	1.6	0.88	593.3	7.5	579	12	564	9	-2
14	1.88	120	834	1408	0.61	0.062	4.1	0.90	2.5	0.098	1.3	0.214	0.8	0.035	1.8	0.53	597.6	7.8	676	90	559	19	13
15	0.13	161	1359	1982	0.71	0.060	0.9	0.85	1.7	0.095	1.3	0.208	0.7	0.028	1.5	0.79	581.2	7.4	593	20	547	9	2

* pontos não utilizados para determinação de idades.

Tabela TS-1: Dados isotópicos U-Th-Pb para zircões do Granito Itaquera (amostra ITA-2) pertencente ao Domínio Embu, dos granitos Itu e Terra Nova (ITU-14X e TN-1), pertencentes ao Domínio Jundiá, e do Charnockito Ubatuba (amostras CHA-1) do Domínio Costeiro.

Spot	%Pb _{total}	²⁰⁶ Pb _{red.}	Th	U	Th/U	²⁰⁷ Pb/	%	²⁰⁷ Pb/	%	²⁰⁶ Pb/	%	²⁰⁸ Pb/	%	²⁰⁸ Pb/	%	²⁰⁶ Pb/	1σ	²⁰⁷ Pb/	1σ	²⁰⁸ Pb/	1σ	%	
	comum	(ppm)	(ppm)	(ppm)		²⁰⁶ Pb	err.	²³⁵ U	err.	²³⁸ U	err.	²⁰⁶ Pb	err.	²³² Th	err.	Rho	²³⁸ U	²⁰⁶ Pb	²³² Th		Discor		
																	idade	idade	idade		dancia		
TN-1- Granito Terra Nova																	Idade intercepto = 579±12 Ma						
1.1	0.34	66.7	1386	876	1.63	0.059	1.4	1.75	6.8	0.097	0.3	0.354	0.7	0.019	1.6	0.05	546	1.7	584	30	377	4	7
2.1	0.10	51.0	711	741	0.99	0.060	1.0	0.86	2.7	0.082	0.3	0.272	0.8	0.022	0.9	0.12	496	1.6	605	23	435	4	22
3.1	3.10	57.5	4264	1746	2.52	0.058	6.7	0.92	6.3	0.043	0.3	0.655	0.5	0.010	0.6	0.05	235	0.9	517	150	180	3	120
4.1	0.43	56.9	954	988	1.00	0.059	1.7	1.49	7.4	0.075	0.3	0.102	1.2	0.007	1.4	0.04	416	1.3	554	37	125	3	33
5.1	0.01	240	3525	2781	1.31	0.059	0.3	0.95	1.7	0.101	0.2	0.385	0.3	0.029	0.4	0.13	616	1.3	579	8	587	2	-6
6.1	2.13	89.7	2640	1863	1.46	0.059	4.6	0.68	1.8	0.057	0.3	0.434	1.3	0.017	1.6	0.16	344	1.1	559	101	299	6	62
7.1	11.4	82.5	10443	3181	3.39	0.067	22.1	0.50	3.7	0.029	0.3	1.115	0.4	0.010	0.5	0.08	170	1.7	847	464	157	5	399
8.1	0.59	86.6	1677	1264	1.37	0.060	1.7	1.12	4.4	0.083	0.3	0.353	0.5	0.021	0.9	0.07	491	1.6	601	37	396	4	22
9.1	2.71	107	2719	3120	0.90	0.057	5.8	0.22	11.1	0.038	0.5	0.364	0.5	0.016	0.9	0.05	246	1.4	480	129	274	6	95
3.2	1.57	56.4	3058	1262	2.50	0.060	3.8	2.09	9.0	0.066	0.3	0.445	0.6	0.009	0.8	0.03	322	1.1	606	83	172	2	88
10	2.71	22.9	686	412	1.72	0.064	7.8	1.42	5.8	0.070	0.5	0.401	2.4	0.015	2.6	0.08	392	2.3	753	166	259	9	92
11	2.57	68.2	2644	1534	1.78	0.062	5.3	1.40	6.9	0.059	0.3	0.353	0.6	0.010	0.7	0.04	317	1.2	673	114	174	4	112
1.2	2.17	51.6	2984	1239	2.49	0.060	4.9	1.86	8.6	0.060	0.3	0.469	0.6	0.009	0.7	0.04	298	1.2	609	107	166	3	104
12	0.18	133	1542	1615	0.99	0.059	0.8	0.87	1.1	0.096	0.3	0.294	0.5	0.028	0.6	0.24	587	1.4	569	17	560	3	-3
13	1.68	78.6	1808	1499	1.25	0.058	3.8	0.86	3.5	0.063	0.3	0.329	0.6	0.016	1.5	0.08	375	1.2	545	85	289	5	45
12	0.50	146	2207	1896	1.20	0.059	1.4	1.01	2.8	0.092	0.3	0.335	0.5	0.025	0.6	0.09	552	1.4	564	30	483	4	2

Tabela TS-1: Dados isotópicos U-Th-Pb para zircões do Granito Itaquera (amostra ITA-2) pertencente ao Domínio Embu, dos granitos Itu e Terra Nova (ITU-14X e TN-1), pertencentes ao Domínio Jundiá, e do Charnockito Ubatuba (amostras CHA-1) do Domínio Costeiro.

Spot	%Pb _{total}	²⁰⁶ Pb _{red.}	Th	U	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb	% err.	²⁰⁷ Pb/ ²³⁵ U	% err.	²⁰⁶ Pb/ ²³⁸ U	% err.	²⁰⁸ Pb/ ²⁰⁶ Pb	% err.	²⁰⁸ Pb/ ²³² Th	% err.	Rho	²⁰⁶ Pb/ idade	1σ	²⁰⁷ Pb/ idade	1σ	²⁰⁸ Pb/ idade	1σ	% Discor dancia
comum	(ppm)	(ppm)	(ppm)																				
ITU-14X - Granito Itu																	Idade intercepto = 591±28 Ma						
1.1	1.94	30.8	491	510	0.99	0.059	4.6	0.82	2.4	0.093	0.4	0.332	0.8	0.031	0.9	0.16	567.3	2.4	579	103	546	12	2
2.1	1.47	12.6	626	442	1.46	0.061	4.6	1.44	5.3	0.087	0.4	0.347	0.9	0.019	1.5	0.08	495.8	2.3	645	99	351	7	30
2.2	0.49	16.1	619	167	3.83	0.059	4.4	8.11	10.9	0.152	0.7	0.511	1.2	0.012	1.5	0.06	541.9	4.0	564	97	231	4	4
3.1	0.43	24.4	212	209	1.05	0.057	2.9	1.05	3.5	0.092	0.6	0.275	1.4	0.024	1.5	0.16	551.1	3.1	504	64	454	9	-8
3.2	1.43	49.5	912	531	1.78	0.063	4.1	1.75	8.2	0.064	0.4	0.260	1.2	0.008	1.4	0.05	332.0	1.5	702	88	140	4	111
4.1	1.62	30.8	920	665	1.43	0.059	4.0	1.38	4.5	0.091	0.3	0.359	0.9	0.022	1.1	0.08	526.7	1.9	573	88	393	7	9
4.2	1.95	44.0	545	388	1.45	0.062	5.6	1.71	5.2	0.098	0.5	0.340	2.6	0.022	3.0	0.10	557.9	3.0	677	121	379	13	21
5.1	0.18	6.01	497	564	0.91	0.059	1.3	0.63	2.6	0.090	0.4	0.304	0.8	0.030	0.9	0.14	559.7	2.0	567	27	596	6	1
5.2	0.08	3.79	179	75	2.48	0.060	4.4	2.46	8.2	0.108	0.9	0.559	1.7	0.021	2.0	0.11	575.5	5.3	603	95	421	9	5
6.1	-0.13	36.6	54	46	1.21	0.064	3.3	0.76	3.1	0.095	1.2	0.383	2.5	0.030	2.8	0.38	586.4	6.7	727	70	604	18	24
7.1	0.79	40.3	460	476	1.00	0.061	3.1	1.09	3.1	0.092	0.4	0.265	1.0	0.024	1.2	0.13	548.7	2.3	630	68	445	8	15
7.2	0.00	4.94	385	496	0.80	0.059	1.1	0.82	1.1	0.095	0.4	0.240	0.9	0.028	1.0	0.36	582.5	2.2	572	23	564	6	-2
6.2	-0.11	11.5	86	62	1.43	0.063	2.4	0.82	2.4	0.093	1.0	0.436	2.0	0.028	2.4	0.42	569.4	5.5	702	50	565	13	23
8.1*	0.05	32.6	181	127	1.48	0.063	2.2	1.11	2.4	0.108	0.7	0.432	1.4	0.031	1.6	0.30	650.1	4.5	708	46	615	10	9
8.2*	14.64	34.2	730	647	1.17	0.057	36.9	0.39	33.8	0.050	0.4	0.621	2.9	0.031	3.0	0.01	313.3	3.8	480	831	313	34	53

* pontos não utilizados para determinação de idades.

Tabela TS-2: Dados de razões Lu-Hf obtidos por LA-HR-ICPMS para as amostras de zircão dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e Charnockito Ubatuba (CHA-1).

Granito Itaquera (ITA-2)

Spot	U-Pb idade	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\epsilon \text{ Hf}(0)$	$\epsilon \text{ Hf}$	T DM	$\epsilon \text{ Hf}$
	(t, Ma)		$\cdot 10^6$		$\cdot 10^6$	(t)		(t)	(Ga)	(TDM)
1.1	594	0.281780	26	0.001618	30	0.281762	-35.1	-22.7	2910	5.6
3.1	594	0.281780	22	0.001927	13	0.281759	-35.1	-22.8	2916	5.6
4.1	594	0.281801	25	0.001597	24	0.281783	-34.3	-21.9	2863	5.8
5.1	594	0.281799	25	0.001215	17	0.281785	-34.4	-21.8	2858	5.8
6.1	594	0.281791	23	0.001643	17	0.281773	-34.7	-22.3	2886	5.7
7.1	594	0.281756	29	0.002100	36	0.281733	-35.9	-23.7	2973	5.4
9.1	594	0.281793	27	0.001902	18	0.281772	-34.6	-22.3	2887	5.7
13.1	594	0.281762	27	0.001748	16	0.281742	-35.7	-23.3	2952	5.4
14.1	594	0.281800	26	0.002199	32	0.281776	-34.4	-22.2	2879	5.7
12.1	594	0.281744	24	0.001308	7	0.281730	-36.3	-23.8	2980	5.3
11.1	722	0.282042	29	0.001229	42	0.282026	-25.8	-10.5	2249	8.0

Tabela TS-2: Dados de razões Lu-Hf obtidos por LA-HR-ICPMS para as amostras de zircão dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e Charnockito Ubatuba (CHA-1).

Charnockito Ubatuba (CHA-1)

Spot	U-Pb idade	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\epsilon \text{ Hf}(0)$	$\epsilon \text{ Hf}$	T DM	$\epsilon \text{ Hf}$
	(t, Ma)		$\times 10^6$		$\times 10^6$	(t)		(t)	(Ga)	(TDM)
2.1	582	0.282287	25	0.000804	4	0.282278	-17.1	-4.6	1773	9.8
3.1	582	0.282268	27	0.001389	36	0.282253	-17.8	-5.5	1829	9.5
4.1	582	0.282303	25	0.000640	7	0.282296	-16.6	-4.0	1733	9.9
11.1	582	0.282348	30	0.000690	5	0.282340	-15.0	-2.5	1634	10.2
12.1	582	0.282287	20	0.000620	4	0.282280	-17.1	-4.6	1768	9.8
13.1	582	0.282358	25	0.001010	22	0.282347	-14.6	-2.2	1618	10.3
9.1	582	0.282314	21	0.000764	2	0.282306	-16.2	-3.7	1711	10.0
10.1	582	0.282307	24	0.001051	13	0.282296	-16.4	-4.0	1734	9.9
7.2	582	0.282259	26	0.000813	4	0.282250	-18.1	-5.6	1836	9.5
8.1	582	0.282231	28	0.000891	4	0.282221	-19.1	-6.7	1901	9.3
5.1	582	0.282275	25	0.000455	9	0.282270	-17.6	-4.9	1790	9.7

Tabela TS-2: Dados de razões Lu-Hf obtidos por LA-HR-ICPMS para as amostras de zircão dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e Charnockito Ubatuba (CHA-1).

Ilha Anchieta (IA-10D)

Spot	U-Pb idade	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\varepsilon \text{ Hf}(0)$	$\varepsilon \text{ Hf}$	T DM	$\varepsilon \text{ Hf}$
	(t, Ma)		$\cdot 10^6$		$\cdot 10^6$	(t)		(t)	(Ga)	(TDM)
1.1	500	0.282333	32	0.000770	12	0.282326	-15.5	-4.8	1717	10.0
2.1	500	0.282250	30	0.000971	20	0.282241	-18.5	-7.8	1908	9.3
3.1	500	0.282285	20	0.000592	7	0.282279	-17.2	-6.4	1822	9.6
4.1	500	0.282395	38	0.001316	20	0.282382	-13.3	-2.8	1591	10.4
5.1	500	0.282351	28	0.001120	9	0.282340	-14.9	-4.3	1686	10.1
6.1	500	0.282302	20	0.000742	17	0.282295	-16.6	-5.9	1786	9.7
7.1	500	0.282258	24	0.000676	5	0.282252	-18.2	-7.4	1883	9.4
8.1	500	0.282283	30	0.001090	31	0.282273	-17.3	-6.7	1837	9.5
9.1	500	0.282268	28	0.000411	16	0.282265	-17.8	-6.9	1854	9.5
4.2	500	0.282298	22	0.000528	1	0.282293	-16.8	-5.9	1791	9.7

Tabela TS-2: Dados de razões Lu-Hf obtidos por LA-HR-ICPMS para as amostras de zircão dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e Charnockito Ubatuba (CHA-1).

Granito Itu (ITU-14X)										
Spot	U-Pb idade	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\epsilon \text{ Hf}(0)$	$\epsilon \text{ Hf}$	T DM	$\epsilon \text{ Hf}$
	(t, Ma)		$\cdot 10^6$		$\cdot 10^6$	(t)		(t)	(Ga)	(TDM)
1.1	591	0.282103	29	0.001103	2	0.282090	-23.7	-11.1	2186	8.3
2.1	591	0.282078	30	0.001361	21	0.282063	-24.5	-12.1	2246	8.0
2.2	591	0.282116	43	0.001451	29	0.282100	-23.2	-10.7	2164	8.3
3.1	591	0.282084	22	0.000794	1	0.282075	-24.3	-11.6	2220	8.1
3.2	591	0.282201	38	0.002418	60	0.282174	-20.2	-8.1	2000	8.9
4.2	591	0.282103	32	0.001673	73	0.282085	-23.7	-11.3	2199	8.2
5.2	591	0.282121	34	0.002888	62	0.282089	-23.0	-11.2	2190	8.2
6.1	591	0.282035	28	0.000818	17	0.282026	-26.1	-13.4	2329	7.7
8.1	591	0.281917	28	0.001206	16	0.281903	-30.2	-17.7	2600	6.7
7.2	591	0.282013	28	0.001001	11	0.282002	-26.8	-14.2	2383	7.5
9.1	591	0.282158	28	0.001123	12	0.282146	-21.7	-9.1	2063	8.7

Tabela TS-2: Dados de razões Lu-Hf obtidos por LA-HR-ICPMS para as amostras de zircão dos granitos Itu (ITU-14X), Terra Nova (TN-1), Itaquera (ITA-2), Ilha Anchieta (IA-10D) e Charnockito Ubatuba (CHA-1).

Granito Terra Nova (TN-1)

Spot	U-Pb idade	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$\pm 2 \sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\varepsilon \text{ Hf}(0)$	$\varepsilon \text{ Hf}$	T DM	$\varepsilon \text{ Hf}$
	(t, Ma)		$\cdot 10^6$		$\cdot 10^6$	(t)		(t)	(Ga)	(TDM)
1.1	579	0.282049	32	0.002680	20	0.282020	-25.6	-13.8	2349	7.66
2.1	579	0.282217	40	0.003649	139	0.282177	-19.6	-8.3	2001	8.93
4.1	579	0.282123	26	0.001881	71	0.282102	-23.0	-10.9	2167	8.32
10.1	579	0.282217	45	0.004078	57	0.282173	-19.6	-8.4	2010	8.89
11.1	579	0.282122	29	0.003646	30	0.282082	-23.0	-11.7	2212	8.16
5.1	579	0.282162	34	0.003727	79	0.282122	-21.6	-10.3	2124	8.48
9.1	579	0.282218	51	0.006379	68	0.282149	-19.6	-9.3	2063	8.70
14.1	579	0.282094	45	0.005208	60	0.282038	-24.0	-13.2	2311	7.80
6.1	579	0.282481	68	0.007700	32	0.282398	-10.3	-0.5	1507	10.7
8.1	579	0.282135	39	0.004344	18	0.282088	-22.5	-11.4	2199	8.20
13.1	579	0.281991	37	0.004907	17	0.281938	-27.6	-16.8	2531	6.99

ITU-14X (Granito Itu)

ITA-2(Granito Itaquera)

Figura FS-1. Diagramas de Concórdia para granitos Itu (ITU-14X), Itaquera (ITA-2), Terra Nova (TN-1), e charnockito Ubatuba (CHA-1).

CHA-1 (charnockito Ubatuba)

TN-1 (Granito Terra Nova)

Figura FS-1. Diagramas de Concórdia para granitos Itu (ITU-14X), Itaquera (ITA-2), Terra Nova (TN-1), e charnockito Ubatuba (CHA-1).

Charnockito Ubatuba (CHA-1)

Charnockito Ubatuba (CHA-1)

Figura FS-2. Imagens de catodoluminescência dos zircões analisados para as razões isotópicas U-Th-Pb e Lu-Hf, com os respectivos pontos amostrados em CHA-1 (charnockito Ubatuba), ITA-2 (Granito Itaquera), IA-10D (Granito Ilha Anchieta), TN-1 (Granito Terra Nova), ITU-14X (Granito Itu).

Granito Itaquera (ITA-2)

Granito Itaquera (ITA-2)

Figura FS-2. Imagens de catodoluminescência dos zircões analisados para as razões isotópicas U-Th-Pb e Lu-Hf, com os respectivos pontos amostrados em CHA-1 (charnockito Ubatuba), ITA-2 (Granito Itaquera), IA-10D (Granito Ilha Anchieta), TN-1 (Granito Terra Nova), ITU-14X (Granito Itu).

Granito Ilha Anchieta (IA-10D)

Granito Terra Nova (TN-1)

Figura FS-2. Imagens de catodoluminescência dos zircões analisados para as razões isotópicas U-Th-Pb e Lu-Hf, com os respectivos pontos amostrados em CHA-1 (charnockito Ubatuba), ITA-2 (Granito Itaquera), IA-10D (Granito Ilha Anchieta), TN-1 (Granito Terra Nova), ITU-14X (Granito Itu).

Granito Itu (ITU-14X)

Figura FS-2. Imagens de catodoluminescência dos zircões analisados para as razões isotópicas U-Th-Pb e Lu-Hf, com os respectivos pontos amostrados em CHA-1 (charnockito Ubatuba), ITA-2 (Granito Itaquera), IA-10D (Granito Ilha Anchieta), TN-1 (Granito Terra Nova), ITU-14X (Granito Itu).