UNIVERSIDADE DE SÃO PAULO INSTITUTO DE GEOCIÊNCIAS

MAGMATIC EVOLUTION, IGNEOUS PETROGENESIS AND METALLOGENETIC IMPLICATIONS OF THE OROSIRIAN MAGMATISM AT THE TAPAJÓS MINERAL PROVINCE, AMAZONIAN CRATON

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Resumo

Muito tem se debatido nos últimos anos quanto ao ritmo de crescimento da crosta continental ao longo das eras geológicas, sendo os modelos existentes variáveis entre crescimento episódico (com picos de produção), ou então de caráter mais contínuo com papel mais relevante do Arqueano. No contexto da Plataforma Sul-Americana, o Cráton Amazônico consiste em uma boa área de estudo quando se refere à crosta Pré-Cambriana, com boas exposições de rochas Arquenas e Proterozóicas parcialmente cobertas por sedimentos siliciclásticos associados às bacias hidrológicas fanerozóicas. Curiosamente, em um contexto global, as associações rochosas e a geodinâmica arqueana, apesar de serem mais raras, têm chamado mais a atenção dos pesquisadores, e o número de publicações referentes ao Arqueano são muito maiores do que as referentes ao Proterozóico. Olhando para a porção centro-sul do Cráton Amazônico, a Província Mineral do Tapajós (PMT) consiste em uma excelente área de estudo, onde predominam intrusões orosirianas (2.0 e 1.87 Ga) muitas das quais associadas à ocorrências e depósitos minerais de metais base e preciosos. Nesse sentido, esse estudo traz considerações petrogenéticas referente às suítes ígneas presentes na PMT bem como as respectivas implicações tectônicas e metalogenéticas para a região. Os resultados permitiram a separação das rochas presentes no Tapajós em dois conjuntos: a sequência magmática antiga (2.0 - 1.95 Ga) e a sequência magmática nova (1.89 – 1.86 Ga). A sequência antiga (OMS na sigla em inglês) é dividida em três subgrupos de acordo com os resultados obtidos.

O grupo I representa os primeiros pulsos de magmatismo na PMT e caracteriza-se por granitos e granodioritos peraluminosos, ferroanos e cálcio-alcalinos, datados em 2011 Ma, caracterizados por ε Nd_(t) evoluído (–8.36) e alta temperatura de saturação em zircão (798°C), características que indicam a contribuição de crosta continental para a formação desses magmas, marcando o início do arco magmático. Os dados de modelamento geoquímico mostram que as rochas do grupo I evoluíram em um trend anidro e oxidado em direção a altas razões La/Yb e Sr/Y através da extração de plagioclásio, piroxênio, biotita, magnetita e titanita. Adicionalmente, a fO_2 dos magmas abaixo de Δ FMQ e a evolução anidra conferem às rochas do grupo I umas baixa favorabilidade para a formação de depósitos magmático hidrotermais de Cu–Au.

As rochas do grupo II são mais variáveis em termos composicionais e representam a evolução do arco magmático. O grupo é marcado por sieno- e monzogranitos, magnesianos a ferroanos, álcali-cálcicos à cálcio-alcalinos, metaluminosos a félsico-peraluminosos, com idade em 1986 Ma e caracterizados por ϵ Nd_(t) moderadamente negativos (de –1 a –3). Modelamento geoquímico mostra que essas rochas evoluíram sob a presença de anfibólio, responsável pela baixa razão Dy/Yb nas bordas dos zircões, e magnetita, que explica a fO_2 até Δ FMQ +4. Esses atributos geoquímicos permitem classificar as rochas do grupo II (e as equivalentes extrusivas) como férteis do ponto de vista metalogenético. De fato, e não surpreendentemente, a maior parte dos depósitos na PMT está hospedado nessas rochas (Tocantinzinho, Chapéu do Sol, São Jorge, Coringa e Patrocínio) onde o minério consiste principalmente em veios e vênulas de pirita e quartzo ±ouro nas alterações sericíticas, potássica e/ou propilítica (com sulfetos disseminados mais raramente).

O grupo III é comparativamente mais raro na PMT, e é composto por quartzo-sienitos e quartzo-monzonitos de alto potássio, ferroanos, alcalinos, metaluminosos a fracamente peraluminosos, de idades que variam de 1993 à 1974 Ma. Modelamento geoquímico mostra uma evolução compatível com K-feldspato, plagioclásios, biotita, apatita, piroxênio e ilmenita, com anomalias negativas de Eu e baixas razões Sr/Y e La/Yb. A evolução reduzida é coerente com os valores de fO_2 abaixo de Δ FMQ +1. Apesar de ser síncrona com as rochas do grupo II, os mecanismos geradores da sequência de alto potássio não é de fácil entendimento. Com base na característica reduzida e anidra dos magmas, a petrogênese das rochas do grupo III possivelmente envolve fusão por descompressão de manto litosférico metassomatizado, possivelmente induzida por corner-flow associado à subducção. Complementarmente, essas rochas em teoria não apresentam as características de magmas formadores de depósitos magmático hidrotermais, entretanto, em campo foi constatado que essas rochas são afetadas por alteração hidrotermal e apresentam mineralização disseminada representada por pirrotita ±ouro presente nas alterações sericítica, potássica e/ou carbonática. Sendo assim, as rochas do grupo III podem ser consideradas férteis devido à interação com os magmas mais hidratados e oxidados do grupo II.

A sequência magmática nova (YMS na sigla em inglês) é representada pelas vulcânicas do Grupo Iriri e pelas rochas graníticas das suítes intrusivas Parauari (PAR) e Maloquinha (MLQ) (e foram descritas nos depósitos V3, Palito e Batalha). As rochas da YMS são mais frequentes na porção leste da PMT. PAR e as vulcânicas do Grupo Iriri representam os primeiros pulsos de magmatismo da YMS, e as rochas são magnesianas a ferroanas, cálcio-alcalinas à álcali-cálcicas e alcalinas, metaluminosas a félsica-peraluminosas. As vulcânicas intermediárias evoluem em direção a altas razões Dy/Yb, Sr/Y e La/Yb através da cristalização de K-feldspato, anfibólio, plagioclásio e biotita. A parte ácida do Grupo Iriri e as rochas graníticas da PAR evoluíram em um trend similar compatível com plagioclásio, K-feldspato, piroxênio, titanita e apatita, em direção a baixas razões Sr/Y, La/Yb e Eu/Eu*, compatível com fontes máficas reduzidas e anidras. As rochas da suíte PAR apresentam εNd_(t) mais fortemente negativos (média de -4.85) quando comparado às rochas do Grupo Iriri, sugerindo um maior tempo de residência em reservatórios crustais. A assinatura geoquímica dos granitos PAR é interpretada como o resultado da fusão de manto metassomatizado em um ambiente tardi- a pós-orogênico. Apesar da característica anidra e reduzida, o contexto tectônico da YMS é adequado para a formação de depósitos magmático hidrotermais ricos em ouro, uma vez que esses magmas eficientemente mobilizam sulfetos previamente formados ricos em elementos siderófilos e calcófilos. MLQ representa os últimos pulsos de magmatismo orosiriano da YMS e é composta essencialmente por álcali feldspato granitos ferroanos, álcali-cálcicos, moderadamente peraluminosos, compatíveis com uma evolução com piroxênio e ilmenita. Esses atributos e os ɛNd(T) perto de zero ou fracamente negativos (entre -2.64 and -0.28) indicam fusão de manto litosférico metassomatizado. Do ponto de vista metalogenético, MLQ apresentam baixa favorabilidade para a formação de depósitos magmático hidrotermais de cobre e ouro.

Palavras-chave: depósitos magmático hidrotermais, Cráton Amazônico, Província Mineral do Tapajós, arco magmático, geoquímica, zircão, geocronologia

Abstract

Continental crust growth ratio has been challenging researchers significantly over the past decades, and the existing models vary from episodic to continuous growth ratios, the latter with a more significant role of the Archean Eon. In the South American Platform, the Amazonian Craton (AC) provides an excellent window into Precambrian continental crust, with many exposure of Archean and Paleoproterozoic continental crust. Interestingly, on a global perspective, Archean tectonics and rockassociations has been targeted more frequently and the number of papers overcomes significantly Paleoproterozoic-related publications. Looking closely to south-central AC, the Tapajós Mineral Province (TMP) consists on an excellent area of study as it comprises multiple Orosirian igneous suites within the 2.0 - 1.87 Ga interval with associated mineral deposits and occurrences of both base and precious metals. Within this aspect, this study provides new petrogenetic constraints on the TMP's igneous suites based on whole-rock and zircon-geochemistry, with the respective tectonic and metallogenetic implications. The results allow the separation of two main age groups within the TMP: the older- (2.0 - 1.95 Ga) and younger magmatic sequences (1.89 - 1.86 Ga). The older magmatic sequence (OMS) is divided into groups I, II and III granitoids that according to the results acquired evolved through fractional crystallization and represents the first batches and evolution of the magmatic arc.

Group I marks the onset of OMS and encompasses ferroan, calc-alkalic and peraluminous granites and granodiorites dated in 2011 Ma, characterized by evolved $\varepsilon Nd_{(T)}$ and high zircon saturation temperature (798°C), all compatible with a strong crustal component on magmatic arc magmas. Geochemical modelling shows a dry and oxidized evolution towards high La/Yb and Sr/Y ratios through extraction of plagioclase, pyroxene, biotite, magnetite and titanite. In addition, zircon-based fO_2 estimates below ΔFMQ combined with their pyroxene-bearing evolution renders group I magmas a low metallogenetic favorability for the formation of magmatic hydrothermal (Cu – Au) mineral deposits.

Group II rocks are compositionally more variable, represent the evolution of the arc magmatism, and comprises magnesian to ferroan, alkali-calcic to calc-alkalic, metaluminous to felsic-peraluminous granodiorites, monzo- and syenogranites of ca. 1986 Ma, characterized by moderately negative $\varepsilon Nd_{(T)}$ (from -1 to -3). Geochemical modelling shows an evolution compatible with amphibole and magnetite extraction, which is also corroborated by low Dy/Yb zircon rims and fO_2 between ΔFMQ +0 and +4. These set of attributes allow group II granites (and its volcanic equivalents) to be considered as metallogenetic fertile for the formation of magmatic-hydrothermal Cu – Au mineral systems. In fact, most rocks from the Tocantinzinho, Chapéu do Sol, São Jorge, Coringa and Patrocínio deposits belong to group II rocks, where mineralization is defined by disseminated gold-bearing sulfides or by pyrite-quartz ±gold ±chalcopyrite veins and veinlets most often found in the sericitic and, less frequently, in the potassic and propylitic alteration zones.

Group III rocks are rarer in the TMP and are defined by high-K, ferroan, alkalic, metaluminous to slightly peraluminous quartz-monzonites and quartz-syenites with ages that vary from 1993 and 1974 Ma. Whole-rock geochemistry shows an evolution coherent with K-feldspar, plagioclase, biotite, apatite, clinopyroxene and ilmenite fractionation, which is accompanied by stronger negative Eu anomalies, Sr and Ba depletion, and low Sr/Y and La/Yb ratios. Its anhydrous and reduced petrologic trend is supported by fO_2 values below $\Delta FMQ + 1$. Despite its synchronicity with group II, group III's petrogenesis is harder to be constrained. In view of their reducing and anhydrous evolution, decompression melting of metasomatized mantle is proposed as the main mechanism for generating group III magmas. Moreover, these rocks should be considered as metallogenetically unfertile (pyroxene- and ilmenite-bearing evolution), yet, on the field syenites and monzonites are often affected by hydrothermal alteration and show disseminated and gold-bearing pyrite and pyrrhotite crysts on the sericitic, potassic and/or carbonatic alteration halos. As a consequence, group III rocks are mineralized as the result of the interaction with the more hydrous, oxidized and fertile group II magmas.

The younger magmatic sequence (YMS) is represented by the Iriri Group volcanics and by the Parauari (PAR) and Maloquinha (MLQ) Intrusive Suites (described on the V3,

Palito and Batalha deposits). Despite their spread on TMP's geologic maps, these rocks are more often spotted on the eastern part of the province. The first pulses of YMS are represented by the PAR granitoids and coeval Iriri volcanics. Both comprise magnesian to ferroan, calc-alkalic to alkali-calcic and alkalic, metaluminous to felsic-peraluminous rocks. Intermediate Iriri rocks evolved towards higher Dy/Yb, Sr/Y and La/Yb ratios through K-feldspar, amphibole, anorthite-rich plagioclase and biotite extraction. Acid Iriri and PAR granitoids evolved on a similar petrologic trend compatible with albiticplagioclase, K-feldspar, pyroxene, titanite and apatite fractionation, that drives the evolving magmas towards lower Sr/Y, La/Yb and Eu/Eu* ratios and suggest anhydrous and reduced mafic sources. PAR granitoids show more strongly negative $\epsilon Nd_{(t)}$ (average of -4.85) when compared with Iriri rocks, indicating a longer period of residence in crustal hot zones. Its geochemistry signature is interpreted as the result of metasomatized mantle melting on a late- or post-orogenic tectonic setting. Despite the anhydrous and reduced characteristic of the magmas, the geologic framework of YMS is adequate for the formation of gold-rich (or gold only) magmatic-hydrothermal mineral deposits, as these magmas efficiently mobilize previously formed, chalcophileand siderophile-rich sulfides. MLQ marks the last pulses of the Orosirian magmatism in the TMP and is characterized by ferroan, alkali-calcic and moderately-peraluminous alkali-granites that evolved on a pyroxene- and ilmenite-bearing trend. These characteristics and the close to 0 or slightly negative $\epsilon Nd_{(T)}$ (between -2.64 and -0.28) indicates metasomatized mantle melting, likely involving the directly underthrusted SCLM. From a metallogenetic perspective, MLQ magmatism show a low favorability for the formation of magmatic-hydrothermal mineral systems.

Keywords: magmatic-hydrothermal mineral deposits, Amazonian Craton, Tapajós Mineral Province, magmatic arc, geochemistry, zircon, geochronology

Summary

PART I

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Thesis structure

Rather than the classic thesis format, this volume is organized with basis on publishedand submitted-papers. Accordingly, the following sections and sub-sections are presented:

Part I – Introduction, Goals, Methods and Geologic Setting

This first part of the thesis comprises an opening section with a brief introduction to magmatic-hydrothermal mineral deposits, with emphasis on the porphyry epithermal class and how important and relevant is the metallogenetic research on ancient and cratonized Pre-Cambrian terrains. The thesis goals, methods and systematic applied and the geologic framework are presented in Part I as well.

Part II – Results

- Part II of the thesis comprises the results acquired during the development of this research, which are presented on published and submitted paper format. Accordingly, Chapter 2 comprises the paper "Orosirian magmatism in the Tapajós Mineral Province (Amazonian Craton): the missing link to understand the onset of Paleoproterozoic tectonics", published on Lithos in January 2020. This paper is based on petrography, whole-rock geochemistry and U-Pb zircon dating. It focuses on constraining the petrogenetic mechanisms behind the 2.0 1.87 Ga igneous suites present in the Tapajós Mineral Province, south-central Amazonian Craton.
- The second part of the results refer to zircon geochemistry data, where in-situ trace-element measurements were used with whole-rock geochemistry database in order to constrain the petrologic evolution of the host-rocks of main mineral deposits within the Tapajós. In addition, the results were also used as proxies of the oxidation state of the hosting magmas, which has

important metallogenetic implications. These results were organized on the paper "Towards the fertility trend: unraveling the economic potential of igneous suites through whole-rock and zircon geochemistry (example from the Tapajós Mineral Province, Northern Brazil)" submitted to Ore Geology Reviews on March 2021.

Part III – Discussion and Conclusions

The final part of the thesis reviews the results acquired and summarizes the main discussion and concluding remarks presented on this research. Additionally, raw zircon trace-element analyses results are provided as supplementary material in the end of this volume.

1. Introduction

Magmatic-hydrothermal mineral deposits are the ultimate result of the interaction between igneous derived fluids and its country rocks. Porphyry Cu ±Au ±Mo deposits in particular, are genetically related with intermediate to acid, oxidized $(\Delta FMQ > 0)$ and hydrous intrusions $(2 - 6 \text{ wt.}\% \text{ H}_2\text{O})$ found in crustal levels no deeper than 5 Km (Sinclair, 2007; Pirajno, 2009; Sillitoe, 2010; Richards, 2011a; Cooke et al., 2013; Loucks, 2014; Sun et al., 2015). The evolution of the system towards shallower stratigraphic levels will generate Au ±Ag high-sulfidation epithermal systems (with eventually more distal intermediate- and low-sulfidation deposits). On a tectonic perspective, these mineralizing systems are more commonly identified in modern magmatic arcs such as in the Andean Cordillera in South-America and, less frequently, in collisional tectonic settings such as southern Tibet. Axiomatically, the tectonic setting and its associated petrogenetic mechanisms will dictate the geochemical characteristic of the igneous suites and, as a consequence, the typology of the genetically associated magmatic hydrothermal mineral system (e.g. Chen et al., 2015). In essence, in order to fully constrain the metallogenetic potential of a given geologic context for the formation of these types of deposits, it is imperative to previously constrain the tectonic setting and magmatic evolution of the igneous suites so potentially ore-forming plutons can be individualized. Certainly, Phanerozoic arcs are much more inviting to explore for porphyry and epithermal deposits than their older (Precambrian) correspondences, considering variables such as level of erosion, weathering profile and superposed metamorphism. Unsurprisingly, world-class porphyry deposits such as Escondida (Cu), Chuquicamata (Cu–Mo), El Teniente (Cu– Mo), Bingham Canyon (Cu–Au–Mo) are found in Phanerozoic arcs or collisional settings (Ballard et al., 2001; Landtwing et al., 2010; Hervé et al., 2012; Muñoz et al., 2012). The increasing demand for copper (and molybdenum) and its importance towards a greener industry, drives the search for new deposits in Precambrian and cratonized terrains mutually promising and challenging (reader is referred to "Copper is the New Oil" report by Goldman Sachs available at goldmansachs.com/insights/podcasts/ episodes/05-18-2021-nick-snowdon.html).

Part I - Introduction, Methods and Geologic Framework

A first order problem involves the framework displayed by ancient terrains, where the arc-related units appear juxtaposed with the collisional, post-collisional, anorogenic and metamorphic sequences, often superposed by strong and deep weathering profiles. In addition, plate tectonics went through significant changes over the geologic record as Earth progressively cooled (e.g. Bédard, 2006, 2018; Condie, 2018), implying in different petrogenetic mechanisms, rock associations and metallogenetic processes. Not surprisingly, orogenic gold deposits are hosted by granite greenstone–belts terrains, are predominantly Archean and found in ancient cratons (Goldfarb and Groves, 2015); Iron-Oxide-Gold-Copper (IOCG) deposits are usually Pre-Cambrian and found close to shear zones and granitoid bodies (Richards and Mumin, 2013); and porphyry Cu–Au–Mo prefer modern subduction zones and magmatic arcs settings, and are usually hosted by intermediate to acid intrusions.

In terms of igneous petrogenesis within the South American Platform (Almeida et al., 2000), the Paleoproterozoic Era is the most expressive regarding new continental crust addition, with one event at 2.3 – 2.1 Ga (Rhyacian); and another at 2.1 – 1.8 Ga (Orosirian) (Sato and Siga Junior, 2002; Giustina et al., 2009). The younger event is well represented in the Amazonian Craton (AC) (Fig. 1) and comprises calcalkaline, high-K calc-alkaline and shoshonitic intrusive and extrusive suites, with the typically Proterozoic anorthosite–mangerite–charnockite–granite (AMCG) rock association (Dall'Agnol et al., 1999; Tassinari and Macambira, 1999; Santos et al., 2000; Alfredo et al., 2010; Valério et al., 2018). The precise tectonic setting and related interpretations vary among the researchers, and a summary is provided in Table 1.

In south-central AC, in an area known as Tapajós Mineral Province (TMP) (Fig. 1), the Orosirian sequence is intimately related with many gold deposits (with lesser copper and molybdenum occurrences) (Santos et al., 2001; Juliani et al., 2002, 2005; Assunção and Klein, 2014; Bettencourt et al., 2016; Borgo et al., 2017;). Most recent publications describe TMP's mineralizations as porphyry-epithermal mineral systems (Juliani et al., 2005; Echeverri Misas, 2015; Tokashiki, 2015; Cassini, 2016; Lopes and Moura, 2019), yet, Intrusion-Related-Gold-Systems (IRGS) (Santos et al., 2001; Villas et al., 2013) and hybrid porphyry–IRGS models have also been proposed (Juliani et al., 2002; Borges et al., 2009; Biondi et al., 2018). Despite the effort over the past years,



Fig. 1. Amazonian Craton and its tectonic subdivision (Santos et al., 2000, 2006). The Tapajós Mineral Province (TMP) geologic map, adapted from Klein et al. (2001), brings the main Orosirian igneous suites and the selected mineral deposits involved in this contribution. Mafic bodies and Phanerozoic units are not colored.

there are still important knowledge gaps that need to be filled so we can constrain the TMP's true economic potential.

In order to enlighten the debate, the central point of this thesis is to constrain the petrogenesis and magmatic evolution of the 2.0 – 1.87 Ga igneous suites within the TMP, and ultimately define which plutons/units and periods should be considered metallogenetic fertile. Within this regard, we use two different datasets, one of these comprises whole-rock geochemistry data, and another with in situ zircon traceelement and U–Pb measurements.

Whole-rock geochemistry provides relevant information on the magmatic evolution of the igneous suites and allows petrogenetic constraints, particularly for granitic rocks. Typical Cu (±Au) porphyry and high-sulfidation epithermal deposits are genetically connected with hydrous and oxidized plutons that are often amphiboleand magnetite bearing. Hence, major elements and REE patterns are key tools to assess the evolution of the targeted plutons. Zircon analyses are extremely relevant in this study not only for revealing the precise timing and tempo behind the Orosirian units, but also for assessing magmatic fO_2 through the Ce⁴⁺/Ce³⁺ proportion, which has important metallogenetic implications (Ballard et al., 2002; Trail et al., 2012). Up to this moment, zircon-based fO_2 constraints have not been published for the TMP and its mineral deposits-hosting plutons. The results, discussion and conclusions presented in this thesis provide a petrogenetic overview on the 2.0 – 1.87 Ga window, with the respective petrologic evolution, tectonic setting and economic potential of the igneous suites.

1.1. Location and Access

The Tapajós Mineral Province is located at the southwestern part of the Pará state and may be accessed through the north or through the south. From north, the biggest city on the region is Itaituba, where it is possible to access the BR-230 road towards south and, afterwards, the BR-163. The BR-163 runs on the NW–SE direction (black dashed line on Fig. 1) and extends through the entire TMP. Cities and smaller

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villages on the BR-163 (Novo Progresso, Moraes de Almeida and Castelo dos Sonhos) were used as base for the fieldtrips, where smaller country roads may be accessed. From the south, the biggest city is Alta Floresta, located on northern Mato Grosso state. From this city, the MT-208 road is accessed on the east direction, towards the Guarantã do Norte city. Once in Guarantã, it is possible to access the BR-163 on the north direction towards the Pará state and the TMP.

1.2. Problematic and thesis' goals

In summary, this study investigates how the igneous suites in the TMP formed, how they evolved, their respective tectonic setting and the given metallogenetic implications. By combining whole-rock geochemistry with in-situ zircon trace element measurements and U–Pb dating, it is possible to constrain the sources, the timing and processes (assimilation and/or fractional crystallization) involved on the formation of the igneous suites. The TMP comprises an area greater than 130.000 km², with dense rainforest cover and rare outcrops. Hence, establishing magmatic correlations is a key step prior to petrogenetic constraints. Tokashiki (2015), for example, identified ca. 1.97 Ga rhyolites in southern TMP that so far have not been correlated with other lithostratigraphic unit. Geochemical modelling plays an important role in this case, as it allows assessing the minerals involved on the evolution of the suites, and whether different samples, outcrops and/or plutons are likely to be cogenetic.

Ultimately, this study elucidates how igneous petrogenesis, magmatic evolution and tectonic context translates into metallogenetic potential for the formation of magmatic hydrothermal mineral deposits. As a result, this contribution could be understood as an important step towards a more robust, unified and holistic metallogenetic model for the base and precious metals mineralizations described in the TMP, south-central Amazonian Craton.

1.3. Analytical methods

The methods involved on the elaboration of this thesis involved, at first, extensive bibliographic review on the Amazonian Craton, TMP's mineralizing systems, magmatic hydrothermal mineral deposits, crustal evolution, Paleoproterozoic magmatism, tectonics, rock association, petrogenesis and geochemistry. A significant part of this study involved the organization of a whole-rock geochemistry database with representative samples from most units identified in the TMP. The data was treated on a quantitative approach in order to avoid misleading interpretations and, a first filtering criteria was based on the MFW diagram after Ohta and Arai (2007). The diagram was idealized with basis on a dataset of igneous rocks and their respective weathered products, where principal component analysis allows the M and F vertices to capture mafic to felsic differentiation sequence, whereas the W apex relates with the degree of weathering. Accordingly, the samples that plot on the center of the diagram and scatter towards the W vertice present a degree of weathering that might disturb their original geochemical signature and, consequently, these samples were excluded from the database. Whole-rock geochemistry was treated with GCDKit (Janoušek et al., 2006) and later used for the geochemical modelling routines.

Geochemical modelling was carried out using GCDKit and further R programming. The method follows the universal mass balance equation:

1)
$$C_0 = FC_L + (1 - F)C_S$$

where C_0 is the initial system composition, F is the fraction of liquid, C_L composition of liquid and C_S the composition of the solids. The methodology consists on the definition of one parental and one differentiated magma. Mass balance equation checks if the chosen samples are compatible with a petrologic evolution trend. It is possible to obtain the composition of differentiated liquids (equation 2) and crystallized minerals or cumulate (equation 3) by rearranging equation 1). This process can be done for any element (*el*) at any given mineral (*min*).

2)
$$C_L^{el} = \frac{C_0^{el} - C_{min}^{el} F_C}{(1 - F_C)}$$

3) $C_S^{el} = \frac{C_0^{el} - F C_L^{el}}{(1 - F)}$

For these cases F_c is the degree of crystallization or proportion of solids. The accuracy of a given model is given by the R² parameter, which by definition is the sum of the differences between the theoretical and real differentiated melts for each element squared, as it follows:

$$R^{2} = (C_{L(calculated)} - C_{L(real)})^{2}$$

The R^2 values closer to 0 imply in models with a better numerical fit. The partition coefficients (K_D) used for calculation of trace elements were taken from Rollinson (1993) and more details and information on the modelling are available at Janoušek et al. (2016).

Trace elements and U-Pb geochronology analyses in zircon grains were performed at the Department of Earth Sciences (ETH – Zürich) using a Thermo Element XR, sector field, single collector ICP-MS coupled to a 193-nm Resolution S155 (ASI) laser ablation system. The later counts with a two-volume Laurin Technic ablation cell fluxed by high-purity He at 0.5 l min⁻¹ rate. The 20 μ m spots were ablated for 30 seconds with a repetition rate of 3 Hz and a laser energy of 2 J cm⁻². Argon was admixed to the aerosol within the ablation funnel (0.96 I min⁻¹) to carry the ablated material for ionization. The integration time per point was 0.662 seconds, and elemental concentration was calculated using the software lolite (Paton et al., 2011). The stoichiometric Si content of zircon (15.2 wt.%) was used as internal standard for trace element quantification and U–Pb data reproducibility was assured by analyses of reference zircon grains (AUSZ7-1, OG-1, Plešovice and 91500). U-Pb and trace element measurements were acquired at the same spot and fractured or metamict domains were avoided or discarded. Zircon trace element results were treated with GCDKit and U-Pb data with IsoplotR (Vermeesch, 2018), results are also available as supplementary material.

1.4. Geologic Framework, Tectonic Division and Evolution of the Amazonian Craton

The Amazonian Craton, hereinafter AC, comprises approximately 4.6 x10⁶ km² within the South American Platform (Almeida et al., 1981, 2000) and defines one of the largest Precambrian terrains on Earth. The AC is delimited by Neoproterozoic mobile belts (Paraguai–Araguaia and Tucavaca) and show thick Phanerozoic sedimentary cover related with the Amazonian drainage system. The first attempts for subdivision, in the early 70's, divided the craton in western, central and eastern blocks (Amaral, 1974). A few years later Cordani et al. (1979) suggested that the AC evolved from an ancient nuclei against which Proterozoic orogens were juxtaposed. According to Cordani's proposal, the AC would comprise the Maroni-Itacaiunas (2.1 - 1.8 Ga), Central Amazonian (>2.1 Ga), Rio Negro–Juruena (1.7 – 1.45 Ga) and Rondonian Provinces (1.4 – 1.1 Ga). However, this model lacks strength as it was essentially based on Rb–Sr isotopes. On the late 80's, Gibbs et al. (1986) published Archean U–Pb ages for the Carajás Province, which afterwards lead Teixeira et al. (1989) to treat it as the Archean nuclei of the AC. Later, Tassinari and Macambira (1999) proposed the craton's subdivision in the Rondonian-San Ignacio, Rio Negro-Juruena, Venturari-Tapajós, Central Amazon and Maroni–Itacaiunas geochronologic provinces.

Shortly after Tassinari and Macambira's model, Santos et al. (2000) published a review on the craton's subdivision and presented a new proposal based on U–Pb and Sm–Nd isotopes. In this new proposal, Santos separates the Carajás region from the Cental Amazon Province, the Maroni–Itacaiunas becomes the Transamazonian Province, the Venturari–Tapajós is hereinafter referred to as Tapajós–Parima Province, the Rio Negro–Juruena is divided into the Rio Negro and Rondônia–Juruena Provinces, and the Sunsás belt is increased on the Brazilian territory. This proposal was updated on 2006, with subtle modifications that are presented on the map of Figure 1. Perhaps the point of most significant divergence between the existing models that concerns this study, refers to the limit between the Tapajós and the Juruena region at southern AC, where the Alta Floresta Mineral Province is located. Whereas Tassinari and

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Macambira's model positions the limit along the Cachimbo Ridge at southwestern Pará, Santos' model extends the Tapajós towards southwest. Juliani et al. (2021) brings a new discussion on the Tapajós and Juruena Mineral Provinces evolution and the respective metallogenetic implications.

Recently, Carneiro et al. (2019) based on deep processed magnetic data proposed a new tectonic setting for the this part of the craton. According to the authors, the craton would be better divided following E–W lineaments (Paleo-suture zones) intrinsically related with the AC's basement. As proposed by the model, the basement would comprise Archean crust that was previously restricted to the Carajás Province, and would extend through the Central Amazon and Tapajós–Parima Provinces. The model was supported by strongly negative ε Nd results (< –8.36) coupled with >2.5 Ga TDM model ages within the Tapajós region (e.g. Sato, 1998; Echeverri Misas, 2015; Cassini, 2016), even though the significance of Sm-Nd model ages for arc-related rocks is dubious. Yet, direct evidence such as inherited Archean zircon cores are restricted to one grain acquired by Santos et al. (2004), dated at 2733 ±9 Ma. A brief summary and the main features of the tectonic provinces of the Amazonian Craton is presented on the following subsections.

1.4.1. Carajás Province

The Carajás Province, eastern AC hosts world-class base-metal deposits related with granitic rocks, ultra-mafic intrusions and metasedimentary sequences with ages that vary from 2.7 to 1.9 Ga. Among the main examples are the N4-N5 and S11D BIF– hosted Fe deposits (16 Gt at 63% Fe, Figueiredo e Silva et al., 2013); the Salobo (1,112 Mt at 0.69% Cu and 0.43 g/t Au) and Sossego (335 Mt at 1.1% Cu and 0.28 g/t Au, ref) IOCG deposits (Schutesky and de Oliveira, 2020); and the Luanga and Lago Grande mafic complexes with Cr–Ni–PGE deposits (Mansur and Ferreira Filho, 2016). The province is tectonically divided into the Rio Maria (Mesoarchean) and Carajás domains (dominantly Neoarchean) structured on the WNW–ESE trend. The Rio Maria domain comprises ca. 3.05 – 2.85 Ga rocks that belong to the Andorinhas Supergroup (greenstone belt) and also encompasses the Caracol and Arco Verde and other <1.88

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Ga A-type affinity granitoids. The Carajás domain is structured on the Xingu and Pium Complex (TTG, migmatites and granulites) and on the Sapucaia greenstone belt. The cover is represented by metavolcano-sedimentary sequences of the Itacaiunas Supergroup, with interlayed basic to intermediate volcanic rocks, and mafic, ultra-mafic and <1.8 Ga granitic intrusions. The late Paleoproteorozoic (ca. 1.8 Ga) A-type magmatism is also present in the Carajás domain (Cigano, Serra dos Carajás and Pojuca granites).

1.4.2. Central Amazon Province

The province comprises intermediate to acid volcanic rocks (Iriri, Surumu, Burro-Burro, Caicara and Iricoumé Group); A-type intrusions related with the ca. 1.88 Ga Uatumã magmatism (Maloquinha, Mapuera and Saracura Intrusive Suites); with later siliciclastic cover (Palmares, Roraima and Urupi groups); and later tholeiitic affinity sills and dykes. Little is known about the province's basement, and Santos et al. (2000) consider it to be essentially Archean. Interestingly, the province truncates the NW trending structures from the Carajás region, implying in slightly younger ages for the Central Amazon Province.

1.4.3. Transamazonian Province

It comprises granite-greenstone belt terrains with collisional and postcollisional granites related with the Transamazonian orogen (2.3 - 2.0 Ga). Isotopic data point to at least four cicles: i) 2.26 - 2.2 Ga; ii) 2.18 - 2.12 Ga; iii) 2.09 - 2.05 Ga; iv) 2.01 - 2.0 Ga. The first two events involve accretion of greenstone sequences and juvenile continental crust. The last two events involve the formation of magmatic-arc and collisional granitoids. The oldest blocks reported in the province are found in the central part of Amapá, and are represented by ca. 2.5 Ga granulites (Santos et al., 2000).

1.4.4. Tapajós-Parima Province

On Santo's and on Tassinari and Macambira's models, the Tapajós-Parima (or Ventuari-Tapajós Province) represents a series of orogenic-belts accreted to the Central Amazon Province. The accretion process would be responsible for the formation of several magmatic-arcs on the 2.0 - 1.89 Ga interval, with <1.88 Ga postorogenic units (Maloquinha and Iriri Group volcanics).

More recent U-Pb dating suggests two age-groups on the TMP region, both characterized by intrusive and extrusive sequences: 2.0 – 1.95 Ga rocks, hereinafter older-magmatic-sequence (OMS); and 1.89 – 1.86 Ga rocks, hereinafter younger-magmatic-sequence (YMS) (Lamarão et al., 2002; Aguja-Bocanegra, 2013; Echeverri Misas, 2015; Tokashiki, 2015; Cassini, 2016; Gutiérrez, 2018). Regardless of the tectonic model and evolution, TMP is vastly dominated by granitic rocks. The main lithostratigraphic units are represented by the: Cuiú-Cuiú Complex (metatonalites and metabasalts); the Creporizão Intrusive Suite (monzo- and sienogranites); Tropas Intrusive Suite (tonalites and granodiorites); Parauari Intrusive Suite (granitic); and the Maloquinha Intrusive Suites (alkali-feldspar and syenogranites) (Santos et al., 2000, 2001, 2004). A few gold deposits and many occurrences described in the TMP, such as the Tocantinzinho, Patrocínio, Batalha and Palito gold deposits are related with the OMS and YMS rocks (Juliani et al., 2002; Echeverri Misas, 2015; Cassini, 2016; Borgo et al., 2017).

Volcanic rocks were reported by Tokashiki (2015) in southern TMP (ca. 1.97 Ga rhyolites), but the majority of the extrusive manifestation in the region belongs to the ca. 1.88 – 1.87 Ga Iriri Group. The later is divided into the Bom Jardim, Salustiano, Aruri and Moraes Almeida formations. The first comprises basalts, andesites, dacites and rhyolites (BADR), with associated pyroclastic deposits representing the pre-caldera rocks association (Juliani et al., 2005). The Salustiano and Aruri formations represent the caldera dynamic, with rhyolitic to dacitic pyroclastic deposits and volcanic breccias. The high- and low-sulfidation epithermal deposits described in the TMP are related with these rocks (e.g. Aguja-Bocanegra, 2013; Juliani et al., 2005). The Moraes Almeida

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Formation comprises rhyolites and trachytic sequences with pyroclastic deposits with A-type geochemical affinity that resembles the Maloquinha signature. Depending on the geographic position, particularly towards the Central Amazon Province, the volcanic rocks from the Iriri Group are also individualized on the Sobreiro, Iriri and Santa Rosa formations. The first comprises high-K calc-alkaline to shoshonitic BADR rock association with pyroclastic deposits. The Iriri Formation is represented by dacites and rhyolites flows and the Santo Rosa Formation comprises fissure controlled volcanism with extensive effusive association and minor coeval, A-type granitic stocks (Juliani and Fernandes, 2010). A summary of the main lithostratigraphic units identified in the TMP, with the respective tectonic setting and associated mineral deposits is presented on Table 1.

1.4.5. Rondônia–Juruena Province

The province is divided into the Jamari and Roosevelt–Juruena domains. The first comprises medium to strongly metamorphosed sedimentary cover and rapakivi granites that represent arc-related and subsequent anorogenic magmatism of ca. 1606 e 1532 Ma (Bettencourt et al., 1999). The Roosevelt–Juruena domain is poorly known, but in summary it comprises arc-related granitoids, volcanic cover (Beneficente, Roosevelt and Colíder groups) and anorogenic magmatism (Teles Pires Suite) within the 1.84 –1.74 Ga age interval. The region guards important metallogenetic relevance as it holds the tin and gold producing Rondonian and Alta Floresta Provinces respectively. The first shows mineralization related with metaluminous and peraluminous, A-type, late-Paleo to Neproterozoic granites, that other than Sn show recoverable resources of W, Ta and Nb (Bettencourt et al., 2016, 1999). The Alta Floresta Province shows Au–Ag magmatic hydrothermal mineral deposits related with calc-alkaline, I-type, metaluminous to peraluminous granitic intrusions of 1.98 – 1.7 Ga (Assis, 2015).

1.4.6. Rio Negro Province

The Rio Negro Province is delimited to the east by the Tapajós–Parima Province and its boundary with the Sunsás belt isn't well established yet. The province is built on the tonalites and granodiorites from the Cauaburi Complex dated at 1798 ±3 Ma e 1796 ±7 Ma (Santos et al., 2006, 2000). The province encompasses different granitic intrusions of 1700 Ma (Marauiá Suite) and the ca. 1540–1510 Ma (Icana and Uaupés suites), interpreted as magmatic arcs (Santos et al., 2000). Collisional to late-collisional magmatism has also been reported and was responsible for lower crust reworking Tiquié and Marié-Mirim suites (Almeida et al., 1977). Mafic to ultramafic intrusions are grouped on the Tapuruquara Suite and is represented by NW–SE trending dyke swarms and late metasedimentary cover belong to the Tunuí Group.

1.4.7. Sunsás and K'Mudku Provinces

The Sunsás Province is located at the southwestern part of the AC and the K'Mudku belt is located at northern AC, both representing the effects of the Greenvillian Orogeny upon the coalescence of the Amazônica and Laurentia paleoplates. Differently than Sunsás, that is represented by at least four orogenic cycles, the K'Mudku belt is understood as an intracratonic shearing zone (Santos et al., 2006, 2000). Among the four orogenic cycles that are encompassed within the Sunsás Province are the Santa Helena, Candeias, San Javier and Nova Brasilândia orogens, each one characterized by granitic magmatism with ages that vary from 1.4 to 1.1 Ga (Geraldes et al., 2001).

Table 1

Summary of the main igneous suites that encompasses TMP's older and younger magmatic sequences

Litho	ostratigraphic Unit	Description	Geotectonic Context (references between brackets)	Hosted mineral deposits (*)
	$ \left(\begin{array}{c} Maloquinha Intrusive \\ Suite (1.87 - 1.86 Ga)^{(2;3;5)} \end{array} \right) $	Biotite syenogranite and alkali-granite	Post-orogenic ^(1;2;3)	-
		 Rhyolite and trachyte (Moraes Almeida fm) Tuff, ignimbrite and volcanic breccias (Aruri fm) 	 Post-collisional/anorogenic ^(5;6) Magmatic-arc/post-orogenic ⁽⁴⁾ 	V3 (Au)
Younger Magmatic Sequence	/ Iriri Group 1.89 - 1.87 Ga ⁽²⁾	 Rhyolite and ignimbrite (Salustiano fm) Andesite, dacite, trachyandesite, latite, rhyolite and ignimbrite (Bom Jardim fm) 	 Magmatic-arc ⁽⁴⁾ Magmatic-arc ⁽⁴⁾ 	Chapéu do Sol (Cu-Mo-Au)**
(YMS)	Parauari Intrusive Suite 1.89 - 1.87 Ga ^(2;3;6)	Biotite-hornblende monzo- and syenogranite, tonalite, granodiorite	Magmatic-arc ^(2;3) ; Post- collisional ⁽⁶⁾	Batalha (Au) Palito (Au-Cu)
	Tropas Suite 1.90 - 1.88 Ga ⁽²⁾	Tonalite and granodiorites	Island-arc ^(2;3)	-
Older	Creporizão Intrusive Suite 1.98 - 1.95 Ga ^(2;3)	Monzo-, syenogranite, granodiorite and tonalite	Magmatic-arc ^(2;3)	Patrocínio (Au) Tocantinzinho (Au)
Sequence (OMS)	Vila Riozinho Formation 2.00 Ga ⁽⁵⁾	Basaltic-andesite, trachyte, rhyolite	Magmatic-arc ⁽⁵⁾	-
	Cuiú-Cuiú Complex 2.04 - 1.99 Ga ^(1;2)	Gneiss, migmatite, granitoids, amphibolite	Island-arc ^(1;2;3) ; Magmatic-arc ⁽⁶⁾	-
	Jacareacanga Group	Quartzites, metapelites, metavolcanics, metachert	Back-arc and trench derived sedime	ents/oceanic crust ^(1;3)

(*) The São Jorge and Coringa deposits haven't been correlated with any TMP lithostratigraphic unit; **The Chapéu do Sol deposit is associated with both older and younger magmatic sequences. (1) Santos et al. (2000); (2) Santos et al. (2001); (3) Santos et al. (2004); (4) Juliani et al. (2005); (5) Lamarão et al. (2002); (6) Juliani et al. (2002).

Results (Lithos publication available as supplementary material, DOI: 10.1016/j.lithos.2019.105350)

Orosirian Magmatism in The Tapajós Mineral Province (Amazonian Craton): The Missing Link to Understand the Onset of Paleoproterozoic Tectonics

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Abstract

The Tapajós Mineral Province (TMP) located at south-central Amazonian Craton is dominated by igneous suites that show geochemical and petrologic evidence of a longlived subduction process accounting for continental crust generation. The process lasted for approximately 100 Ma and yielded in different intrusive and extrusive manifestations within the 1.99 – 1.89 Ga interval. At its initial stage, arc magmatism is characterized by a strong crustal component on the magmas possibly due to subcrustal-erosion upon the onset of subduction. After this phase, metaluminous primary melts provided by the subduction zone gradually differentiate to peraluminous compositions, the case for the ca. 1.98 - 1.95 Ga Creporizão Intrusive Suite (CRP) and its extrusive correspondences. Geochemical modelling reveals that the first bursts of magmatism at the TMP (at ca. 1.99 Ga) evolved through pyroxene fractionation, whereas the following pulses are amphibole-bearing. As the arc evolves, the mantle wedge gets progressively metasomatized and hydrated, eventually melting to generate the high-K metaluminous to mildly peraluminous granitoids of the ca. 1.89 Ga Parauari Intrusive Suite (PAR), accompanied by more evolved ɛNd_(1.88). The first pulses of the Iriri Group volcanism are synchronous with PAR, nevertheless, Nd isotopes point to different sources. Around 1.87 Ga, slab break off provokes asthenospheric upwelling, which is responsible for destabilizing and melting of the subcontinental lithospheric mantle severely metasomatized by the previous magmatic events, generating shoshonitic and metaluminous melts with variable degrees of crust assimilation, translated into mildly negative $\epsilon Nd_{(1.86)}$ of the Maloquinha Intrusive Suite (MLQ) and Iriri volcanic rocks at an early-anorogenic tectonic setting. Geochemical modelling and the depletion in Ba, Sr and Eu of MLQ and part of Iriri are compatible with early extraction of plagioclase and support the relatively dry evolution of these units. In addition, fractional crystallization alone cannot account for the geochemistry variability of MLQ and Iriri, reinforcing crust assimilation on their petrogenesis. In terms of metallogenetic potential, CRP and PAR have petrologic evolutions consistent with amphibole and magnetite crystallization, pointing to hydrated and oxidized magmas that might be considered as favorable for the formation of magmatic hydrothermal mineral deposits (porphyry Au-Cu-(Mo) and epithermal systems). Lastly, the magmatic events younger than 1.89 Ga might act incorporating residual Aurich sulfide from the mantle, explaining the Au-only characteristic of many mineral deposits described at the TMP.

3. Results (submitted to Ore Geology Reviews)

Towards the fertility trend: unraveling the economic potential of igneous suites through whole-rock and zircon geochemistry (example from the Tapajós Mineral Province, Northern Brazil)

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Abstract

Magmatic hydrothermal mineral deposits axiomatically frame the hosting pluton and the given tectonic setting in which they are inserted. Unsurprisingly, Precambrian porphyry deposits appear to be different than Phanerozoic examples, as collisional or post-collisional deposits are different than arc-related mineralizing systems. As such, this contribution assesses the tectonic framework and the magmatic evolution of the igneous suites present in south-central Amazonian Craton (Tapajós Mineral Province, TMP), and how these parameters translate into metallogenetic potential for the formation of magmatic-hydrothermal copper, molybdenum and gold deposits. For this purpose we gathered whole-rock geochemistry data from selected TMP copper and gold deposits and present new in situ trace-element and U–Pb analyses in zircon.

The host rocks of the selected mineralizing systems belong either to the older magmatic sequence (OMS, 2.00 - 1.95 Ga), or to the younger magmatic sequence (YMS, 1.90 - 1.86 Ga). Whereas OMS presents characteristics of arc-related rocks, YMS

represents the evolution towards post-orogenic or collisional setting. OMS might be divided into groups i, ii and iii granitoids. Group i comprises granites and granodiorites that mark the onset of the arc-magmatism in the TMP at ca. 2011 Ma. In this stage rocks are peraluminous, ferroan, anhydrous, show a strong crustal component and fO_2 values close to or below the fayalite-magnetite-quartz buffer (Δ FMQ), yielding metallogenetic unfertile pluton. These rocks correlate with the Cuiú-Cuiú Complex and comprise samples from the Patrocínio and Tocantinzinho deposits. Group ii granitoids correlate with the Creporizão Suite and comprise Tocantinzinho, São Jorge, Chapéu do Sol and Patrocínio deposit samples (with extrusive equivalents in the Coringa deposit). Rocks are metaluminous to peraluminous, magnesian to ferroan and mark the evolution of the magmatism towards more oxidizing ($0 \le \Delta FMQ \le + 4$), hydrous and metallogenetically fertile conditions at ca. 1986 Ma. Mineralized zones are defined by gold bearing sulfide veins and veinlets within the potassic or sericitic alteration halos. Group iii comprises rarer high-K, metaluminous, ferroan, anhydrous and reduced syenites and monzonites dated at 1993 and 1974 Ma, generated by decompression melting of metasomatized mantle. By itself, group iii rocks should be considered as unfertile batches of magma, however, its interaction with the coeval, more hydrous and oxidized group ii melts, confer these magmas their metallogenetic potential. Mineralization in group iii rocks is defined by disseminated pyrrhotite-pyrite ±gold within the sericitic, chloritic and/or carbonate alteration zones.

YMS comprises intermediate and acid rocks that belong to the Parauari Intrusive Suite and to the Iriri Group. Whereas, intermediate volcanics from YMS evolved on a hydrous and reduced petrologic trend, acid volcanics and the Batalha and Palito granitoids evolved on a dry and reduced trend, reflecting a change on TMP's tectonic context, from magmatic-arc to a post-orogenic or collisional tectonic setting. Despite the reduced and anhydrous characteristic of the magmas, YMS's metallogenetic potential is related with remobilization or melting of SCLM or lower crustal Au-rich sulfides formed on the previous magmatic events. Hence, the first pulses of the YMS might be considered as potentially fertile for the formation of Au-rich magmatichydrothermal deposits.

3.1. Introduction

The metallogenic process requires the presence of fertile rocks that provide not only metals but also ligands, fluids and the volatile contents necessary to form an anomalous concentration and define a mineral deposit. Magmatic-hydrothermal mineral systems, particularly the copper and gold porphyry-epithermal class, are genetically connected with oxidized (Δ FMQ > 0), hydrous (2 – 6 wt.% H₂O), subductionrelated, intermediate to acid igneous suites, intruded at shallow depths (Cooke et al., 2013; Loucks, 2014; Pirajno, 2009; Richards, 2015a, 2011a; Sillitoe, 2010; Sinclair, 2007; Sun et al., 2015). Despite the occurrence of porphyry deposits at collisional and at extensional settings (Chen et al., 2015; Richards, 2015b, 2014, 2009; Wang et al., 2018), it is unquestionable that these deposits occur preferentially at destructive plate margins. Therefore, at a given geologic context, it is important in terms of prospective criteria, to identify which igneous suites are directly related with the magmatic-arc. This separation is straightforward in Phanerozoic subduction zones such as seen in the Andean Cordillera or in the west Pacific rim. The problem arises when we look at ancient and cratonized terrains, where the arc-related sequence appears juxtaposed with the collisional, post-collisional and anorogenic units. A first order problem in this case, is that not all arc-magmas are prone to form magmatic-hydrothermal mineral deposits, even though the reason, processes and features that render a given magmatic system fertile or not are still unclear (e.g. Zhang and Audétat, 2017). The physiology of ancient subduction-zones is not particularly helpful and characteristics such as the absence or diffuse suture zone and ambiguous geochemical signature due to metamorphism and/or weathering are common caveats. Additionally, whereas fluid-flux mantle melting is easily achieved in modern subduction zones, yielding hydrous and metallogenetic fertile magmas, the tectonic and petrogenetic mechanisms behind Paleoproterozoic (or older) rocks are still dubious. Despite these peculiarities, the Archean Spinifex Ridge (Mo-Cu) located at eastern Pilbara Craton (Huston et al., 2007), the Paleoproterozoic Malanjkhand deposit (Cu-Mo-Au) at central India (Stein et al., 2004) and the Aitik Cu-Au-Ag deposit in northern Sweden (Wanhainen et al., 2012) are good examples of high-tonnage Precambrian porphyry deposits.

Within this topic, the south–central portion of the Amazonian Craton, a region known as Tapajós Mineral Province (TMP) consists on a promising area (Fig. 1). It comprises arc-related, collisional and post-collisional igneous suites, that distribute within the 2.0 – 1.86 Ga age interval and host gold (copper and molybdenum in a lesser extent) mineral deposits (Borgo et al., 2017; Juliani et al., 2005; Lamarão et al., 2002; Santos et al., 2004, 2001). Most recent papers describe TMP's mineralizations as porphyry–epithermal mineral systems (e.g. Cassini, 2016; Echeverri Misas, 2015; Juliani et al., 2005; Lopes and Moura, 2019; Tokashiki, 2015), yet, Intrusion-Related-Gold-Systems (IRGS) (Santos et al., 2001; Villas et al., 2013) and hybrid porphyry–IRGS models have also been proposed (Biondi et al., 2018; Borges et al., 2009; Juliani et al., 2002). Despite the effort over the past years, there are still important knowledge gaps that need to be filled so we can constrain the TMP's true economic potential.

Ergo, the central point of this study is to investigate how the host rocks of different mineral deposits at the TMP evolved, examine their general geochemistry characteristics, pinpoint the main differences and similarities and elucidate how and why these magmas became fertile. The data approach given by Loucks (2014), for example, where the author constrains the fertility of plutons by looking at their geochemical signature (i.e. copper-producing plutons show higher whole-rock Sr/Y and V/Sc ratios, used as proxies to the hydrous condition of the magmas) is rather pertinent for our purpose. In this regard, we gathered information and organized a geochemistry database for selected Au-Cu-Mo mineral deposits and occurrences identified in the TMP. In addition, we provide new U–Pb and trace-element analyses in zircon grains from samples collected at central TMP to assess the magmatic evolution of the intrusions. Cerium content in zircon is used to estimate the oxygen fugacity of the rocks and consequently their metallogenetic potential (i.e. typical porphyry deposits are genetically related with plutons with fO₂ greater than the fayalitemagnetite-quartz oxygen buffer (Richards, 2015a). Ultimately, by combining both empirical and theoretical approaches, our purpose is to establish a prospective criteria and a systematic capable of constraining the metallogenetic potential of different igneous suites not only from the TMP, but also from other cratonic terrains.
3.2. Geologic Framework of the Tapajós Mineral Province

The Tapajós Mineral Province (TMP) is part of the south-central Amazonian Craton (AC), on the limit between the Ventuari-Tapajós or Tapajós-Parima and Central Amazonian tectonic provinces (Santos et al., 2000; Tassinari and Macambira, 1999). According to Santos' tectonic model (Fig. 1), the Tapajós-Parima Province is the result of a Paleoproterozoic collisional-orogen that, among other consequences, was responsible for the expressive orogenic and post-orogenic magmatism that predominates in the region. This model has been revisited by many authors over the past years. More recently, Carneiro et al. (2019), supported by high-resolution magnetometry data, claim that the magmatic-arc sequence was built on Archean basement, previously restricted to the Central Amazonian and Carajás Provinces. According to the authors, NNW-SSE lineaments that agrees with Santos' model are intrinsically related with the shallower crustal levels, whereas deeper (>15 km) E-W trending lineaments are related with the Archean basement, which led the authors to suggest an alternative crustal framework for this part of the AC.

3.2.1. Lithostratigraphy

In general, the older units described at the TMP represent different stages of the arc magmatism, whereas the tectonic affinity of the younger sequence remains less consensual (Table 1 presents a summary of TMP's lithostratigraphic units). The igneous suites within the 2.0 – 1.95 Ga age interval, addressed hereafter as the older magmatic sequence (OMS), encompasses: the Cuiú-Cuiú Complex (tonalites and granodiorites of ca. 2.04 - 1.99 Ga); the Vila Riozinho Formation (basaltic-andesite, trachyte, rhyolite of 2.0 Ga); and the Creporizão Intrusive Suite (granitoids of ca. 1.98 - 1.95 Ga, ages after Lamarão et al. 2002; Santos et al., 2004, 2001, 2000).

Approximately 50 million years separate the OMS from the younger magmatic sequence (hereafter YMS). The Tropas and Parauari Intrusive Suites (1.90 – 1.87 Ga) mark the onset of the younger magmatism, characterized by tonalite and granodiorites, with syeno-, monzogranites and acid volcanics for the later. These are

followed by the volcanic rocks of the Iriri Group and its subdivisions, accordingly: Bom Jardim Formation (intermediate to acid volcanics with subordinate ignimbrites of 1.89 – 1.88 Ga); Salustiano and Aruri Formations (rhyolites, ignimbrites of dacitic composition and volcanic breccias of 1.88 – 1.87 Ga); and Moraes Almeida Formation (rhyolites and trachytes of ca. 1.88 Ga, ages and descriptions after Dall'Agnol et al., 1999; Juliani et al., 2005; Lamarão et al., 2002; Santos et al., 2000)). Often, YMS volcanics define dykes or lava flows covering OMS plutons. The Maloquinha Intrusive Suite represents the last stage of YMS and comprises syeno- and alkali-feldspar granites of ca. 1.87 Ga (Lamarão et al., 2002; Santos et al., 2002) that define round shaped plutons.

3.2.2. Typology and General Features of the Mineralizing Systems at the TMP

The results presented in this contribution refer to selected mineral deposits chosen in order to cover most part of the TMP. Accordingly, the Batalha, V3 and Chapéu do Sol gold deposits are found in northern TMP; central TMP is represented by the Tocantinzinho, Palito and São Jorge gold mineralizations; and the Patrocínio and Coringa gold deposits are found in southern TMP. The Patrocínio, Tocantinzinho and Coringa deposits are hosted by the OMS, the first two by ca. 1.97 Ga granitoids that correlate with the Creporizão Intrusive Suite, and the latter is found within coeval volcanics. The Batalha, Palito and V3 deposits are hosted by YMS granitoids and volcanic breccias (the case for the later), whereas the São Jorge and Chapéu do Sol deposits are uniquely associated with both magmatic sequences (Echeverri Misas, 2015; Lamarão et al., 2002). Table 2 summarizes the main features of the mineral deposits selected at this study.

3.2.2.1. Deposits Within the Older Magmatic Sequence (OMS)

The Patrocínio gold mineralization (southern TMP) is found in strongly hydrothermalized (K-metasomatism and sericitic alteration), calc-alkalic, metaluminous to peraluminous, syeno- and monzogranites of ca. 1.97 Ga (Figs. 2a -2i), into which gold bearing sulfide veins and veinlets are injected (Cassini, 2016). A disseminated type of mineralization was also identified and is associated with syenites and monzonites (Figs. 2j – 2m) affected by sericitic, chloritic and carbonate hydrothermal alterations, where the mineralization is characterized by the assemblage pyrrhotite-pyrite ±gold, with traces of chalcopyrite. On the distal zones, barren propylitic alteration was identified and commonly overprints the potassic and sericitic alterations. Even though the Patrocínio mineralization has many attributes of porphyry systems, the magmatic-hydrothermal system still requires additional efforts for a better understanding and a more detailed comprehension.

The Tocantinzinho gold deposit (central TMP), the largest at the TMP with 1.7 million oz. of gold (Borgo et al. 2017), presents a similar geologic framework. It is hosted by metaluminous to peraluminous monzogranites, granitic breccias, aplite and pegmatites of ca. 1.98 Ga, that are affected by an early stage of K-metasomatism, followed by sericitic, chloritic and carbonatic alterations (Biondi et al., 2018; Lopes and Moura, 2019). In this context the mineralization is intimately related with the sericitic alteration and is represented by disseminated gold or quartz-sulfide, gold bearing veinlets. The most common sulfide is pyrite, however, late forming chalcopyrite, sphalerite and galena have also been reported. Biondi et al. (2018) claim that the Tocantinzinho's magmatic-hydrothermal system shows features that resemble both intrusion-related-gold-systems (IRGS) and gold-rich porphyry deposits. Lopes and Moura (2019), on the other hand, are more emphatic and describe the deposit as a "porphyry-style" mineralization since it lacks typical features of Phanerozoic (*stricto sensu*) porphyries.

The Coringa deposit (southern TMP) is hosted by volcanic rocks of ca. 1.97 Ga (Fig. 2n), with minor intrusive bodies that are coeval with the Creporizão Intrusive

Suite. According to Tokashiki (2015) the volcanic units are dominantly rhyolites and the volcanoclastic sequence is represented by volcanic-breccias, lithic-, lapilli- and crystaltuffs, with subordinated ignimbrites. The mineralization is hosted by sericitic altered rhyolites, that define topographic domes, and is focused on brittle structures represented by quartz bearing veins and veinlets with galena, pyrite, chalcopyrite and gold (Fig. 2o). Due the presence of adularia and Mn-carbonates on the mineralized vein, the author describes the Coringa deposit as a low-sulfidation system that evolves to an intermediate-sulfidation, and don't discard the potential of a deeper and genetically connected porphyry system. Measured and indicated reserves sum a total of 516.000 oz. of gold (Tokashiki, 2015).

The Chapéu do Sol (copper, molybdenum and gold) mineralization (northern TMP) is genetically related with volcanic and volcanoclastic sequences, with coeval porphyry and granitic stocks, formed in two age intervals: one at 1.99 – 1.97 Ga and a 100 Ma younger one, at 1.88 – 1.86 Ga (Echeverri Misas, 2015). The high-K affinity of the igneous suites led the author to suggest a mature arc tectonic context. The mineralization is represented by disseminated sulfide (pyrite, chalcopyrite, molybdenite and sphalerite), or gold bearing sulfide veins and veinlets, more frequently found on the sericitic alteration halos with adularia. Echeverri Misas (2015) describes the Chapéu do Sol mineralization as a low-sulfidation system.

3.2.2.2. Deposits Within the Younger Magmatic Sequence (YMS)

Among the deposits hosted by the YMS, the Batalha, Palito and São Jorge are hosted by biotite and amphibole bearing syeno- and monzogranites, whereas the V3 is hosted by intermediate to acid volcanic rocks.

The Batalha gold deposit (northern TMP) is a magmatic-hydrothermal system hosted by granitoids of 1.88 Ga that correlate with the Parauari Intrusive Suite (Juliani et al., 2002). The hydrothermal system is characterized by early Na-metasomatism, followed by potassic, propylitic and late sericitic alterations (the latter two the most

important for the mineralization). Within the propylitic zone, ore consists in disseminated pyrite with gold inclusions, or gold bearing quartz veins with carbonate, fluorite, pyrite, chalcopyrite and chlorite. On the sericitic zone, gold mineralization is found either on fissures or in pervasive style with quartz, sericite, pyrite, chalcopyrite and galena. As proposed by Juliani et al. (2002) the Batalha hydrothermal system is compatible with a porphyry Au-Cu deposit, with some features of IRGS.

The Palito gold and copper deposit (central TMP) is hosted by ca. 1.88 Ga granitoids that according to Echeverri Misas (2015) correlates with the late stages of the Parauari Intrusive Suite, on a collisional or post-collisional tectonic setting. It presents potassic, propylitic and sericitic hydrothermal alteration zones and mineralization consists mainly on sulfide bearing, NW-SE and E-W trending quartz veins and veinlets within the sericitic alteration halo, with less frequent disseminated sulfides (Figs. 2p - 2t). Chalcopyrite is the main sulfide associated with the gold mineralization, but pyrite, galena, pyrrhotite and Bi bearing minerals were also identified. Echeverri Misas (2015) describes this magmatic-hydrothermal system as a porphyry Au-(Cu) deposit.

The São Jorge gold deposit (central TMP) is hosted by the homonymous granite that was divided by Lamarão et al. (2002) on the older and younger São Jorge granites (1.98 and 1.89 Ga respectively), the latter more closely related with the mineralization. Similarly to the Batalha deposit, it shows mineralization focused on the propylitic and sericitic alteration halos, where gold is usually associated with pyrite veins and veinlets. A disseminated type of mineralization is also identified but is comparatively rarer. Other than pyrite chalcopyrite, sphalerite, molybdenite and galena were also described (Borges et al., 2009; Lamarão et al., 2002). Borges et al. (2009) claim that the deposit has geological attributes of both IRGS and porphyry systems.

Differently than the other YMS hosted deposits, the V3 gold mineralization (northern TMP) is associated with hydrothermal breccias developed on the volcanic and volcanoclastic sequence of the Iriri Group (1.89 - 1.87 Ga), with coeval shallow level granitic stocks. The hydrothermal system comprises pervasive and fissural potassic, silicic, propylitic, sericitic, argilic and advanced argilic alunite bearing

alterations. The latter hosts the highest gold contents, however, the potassic, propylitic and sericitic alteration zones also show considerable sulfide contents. 40 Ar/ 39 Ar dating in alunite crystals acquired by Echeverri Misas (2015) yielded 1.86 – 1.84 Ga, which is interpreted as the age of mineralization. The author describes the deposit as a high-sulfidation epithermal system.

In fact, YMS volcanic rocks are often found as dykes in OMS granitoids (the association has been reported in the Tocantinzinho, Patrocínio and Palito deposits) and potentially define an additional type of mineralization, characterize by gold bearing pyrite veins and veinlets injected along the contact between the intrusive and subvolcanic units (Fig. 2u).

Table 2

Host rocks, mineralizing style and hydrothermal alteration evolution of the selected TMP mineral deposits.

Deposit/ Minoral	Host Rocks	Mineralization Style			Deferences					
occurrence			Sodic	Potassic	Propylitic	Sericitic	Argilic	Adv. Argilic	References	
V3 (Au)	1.89 - 1.87 Ga volcanic rocks (Iriri Group)	Hydrothermal breccias and veins	ΡI	Kfs, Amp, Bt, Qz, ±Hm ±Sul	Pl, Kfs, Qz, Ser, Chl, Ep, Cab ±Amp ±Sul	Qz, Dk, Ser, Chl, ±Alu ±Sul	Dk, Kao, Ser, Chl, ±Pl ±Kfs	Pyr, Alu, Dsp, Rt, And, Sul, Cu, Ag, Au, ±Hm ±Dk ±Kao	Echeverri Misas (2015)	
Palito (Au - Cu)	1.88 Ga granitoids	Veins and disseminated	Pl, Bt, ±Kfs ±Amp ±Qz	Kfs, Qz, ±Pl ±Amp ±Bt ±Hm	Pl, Ser, Chl, Ep, Ttn, Cab ±Sul	Pl, Kfs, Qz, Ser, Sul ±Au ±Cu	Pyr, Kao, Ser, Sul ±Pl ±Kfs	-	Echeverri Misas (2015)	
Batalha (Au)	1.88 Ga granitoids	Veins and disseminated	PI	Kfs, Bt, Qz	Pl, Chl, Ep, Cab, Sul, ±Qz ±Au	Qz, Ser, Sul, Au, Fl ±Cab	-	-	Juliani et al. (2002)	
São Jorge (Au)	OMS and YMS granites	Veins and disseminated	Qz, Pl, Kfs, Bt, Ttn, Mag		Pl, Bt, Chl, ±Ep ±Cab ±Ser ±Sul ±Mag ±Qz ±Kfs	Qz, Cab, Sul, Ser ±PI ±Kfs ±Bt	-	-	Lamarão et al. (2002); Borges et al. (2009)	
Chapéu do Sol (Cu - Mo - Au)	OMS and YMS volcanics and subvolcanics	Disseminated, veins and veinlets	PI	PI, Bt, Kfs, Qz	Pl, Qz, Chl, Ep, Rt, Ttn, Sul, Cab, ±Hm ±Amp	Qz, Ser, Adu, Sul, Au, ±Ttn ±Cab ±Bt	Qz, ill, Kao ±Hm	-	Echeverri Misas (2015)	
Patrocínio (Au)	1.99 - 1.95 Ga granites, syenites and monzonites	Veins and veinlets ±disseminated	PI	Kfs, Qz	Chl, Ep, sodic-Pl	Ser, Py, Po, ±Au	Chl, ±Ccp	-	Cassini (2016)	
Tocantinzinho (Au)	1.98 Ga granites	Disseminated and veinlets	-	Kfs, Qz, Pl, Ep, Chl, Py, Ccp, Au ±Hm		Ser, Py, Au, Qz, Ccp, Gn, Sp, ±Hm ±Pl	-	-	Borgo et al. (2017); Lopes and Moura (2019); Biondi et al. (2018)	
Coringa (Au)	1.97 rhyolites	Veins and veinlets	-	Kfs, Bt, ±Qz	Chl, Ep, Qz, Pl, ±Cab ±Py	Qz, Ser, Ccp, Sp, Gn, ±Adu	ill	-	Tokashiki (2015)	

Adu: adularia; Alu: alunite; Amp: amphibole; And: andalusite; Bt: biotite; Cab: carbonate; Ccp: chalcopyrite; Chl: chlorite; Dk: dickite; Dsp: diaspore; Ep: epidote; Fl: fluorite; Gn: galena; Hm: hematite; ill: illite; Kao: kaolinite; Kfs: K-feldspar; Mag: magnetite; Pl: plagioclase; Po: pyrrhotite; Py: pyrite; Qz: quartz; Rt: rutile; Ser: sericite; Sp: sphalerite; Sul: sulfide; Ttn: Titanite.



Fig. 2. Typology of the different OMS (a - o) and YMS rocks (p - u). (a) Massive, leucocratic, granodiorite drill core sample. (b) Massive, partially altered (potassic alteration), granodioritic porphyry; (c) Porphyritic and massive syenogranite with compositionally zoned plagioclase phenocrysts; (d) Syenogranitic porphyry with plagioclase phenocrysts (outcrop near the Patrocínio area); (e) Equigranular, massive monzogranite; (f) Strongly altered (potassic alteration) granite, with gold bearing pyrite

in chlorite-sericite veinlets; (g) Sulfide bearing, chlorite-sericite alteration in Kmetasomatized granitoid; (h) Gold bearing, quartz sulfide vein injected near the granite-syenite contact. Rocks have previously experienced pervasive potassic and subsequent chlorite-sericite alteration; (i) Granite drill-core sample with multi-phasic hydrothermal events. early potassic alteration (reddish feldspar crysts) is followed by fissural and interstitial chlorite-sericite alteration (gray-greenish color). The last hydrothermal event is represented by the white-silica infilled breccia; (j) Drill core sample with contact between monzonite (left) and monzogranite (right) with a reaction rim (central) and small opaque (sulfide?) crysts; (k) Potassic and chloritesericite altered syenite; (I) Chlorite-sericite and potassic altered monzonite with disseminated, gold bearing sulfide (pyrite and pyrrhotite), and less frequent sulfide veinlets; (m) Aplitic syenite found as synplutonic dykes in OMS granites. (n) Rhyolite with feldspar phenocrysts and potassic alteration form the Coringa deposit; (o) Coringa deposit ore example, with strongly sericitic altered volcanic rock (rhyolite?) cross-cut by a chalcopyrite + sphalerite + galena vein, brecciated by sericitic + white silica alteration. (p - t) Palito deposit samples (examples from Echeverri Misas, 2015; (p) potassic altered granite with secondary K-feldspar; (q) potassic and propylitic alteration with K-feldspar, chlorite, epidote and carbonate (Cal); (r) Sericitic alteration with quartz (Qtz), sericite (Ser) and pyrite (Py); (s) Sulfide vein in strongly hydrothermalized granite (5), with (1) chalcopyrite, (2) pyrite, (3) breccia zone and (4) quartz veins; (t) Strongly hydrothermalized granite with fluorite (6) and white silica veining (7). (u) OMS granite injected by YMS dacite dyke with white silica, gold bearing sulfide pocket and smaller veinlets along the dyke contact.

3.3. Methods

The results presented in this contribution refer to whole-rock and zircon geochemistry/isotopic analyses. The whole-rock geochemistry database counts with published and unpublished results from selected deposits in order to cover most part of the TMP, and involves results from Biondi et al. (2018), Cassini (2016), Echeverri Misas (2015), Gutiérrez (2018), Juliani et al. (2002), Lamarão et al. (2002), Lopes and Moura (2019) and Tokashiki (2015) (geochemistry database is available as supplementary material).

Whole-rock geochemistry data was treated with GCDKit (Janoušek et al., 2006) and modelling routines of fractional crystallization were performed using further R programming (Janoušek et al., 2016). Major elements were modeled through simple

mass-balance and trace-elements through Rayleigh crystallization using partition coefficients from Rollinson (1993) and GERM database (available at <u>http://earthref.org</u>).

Trace-elements and U-Pb geochronology analyses in zircon grains were performed at the Department of Earth Sciences (ETH - Zürich) using a Thermo Element XR, sector field, single collector ICP-MS coupled to a 193-nm Resolution S155 (ASI) laser ablation system. The later counts with a two-volume Laurin Technic ablation cell fluxed by high-purity He at 0.5 I min⁻¹ rate. The 20 μm spots were ablated for 30 seconds with a repetition rate of 3 Hz and a laser energy of 2 J cm⁻². Ar was admixed to the aerossol within the ablation funnel (0.96 I min⁻¹) to carry the ablated material for ionization. The integration time per point was 0.662 seconds, and elemental concentration was calculated using the software lolite (Paton et al., 2011). The stoichiometric Si content of zircon (15.2 wt.%) was used as internal standard for trace element quantification and U-Pb data reproducibility was assured by analyses of reference zircon grains (AUSZ7-1, OG-1, Plešovice and 91500). U-Pb and trace element measurements were acquired at the same spot, and fractured or metamict domains were avoided. Zircon trace element results were treated with GCDKit and U-Pb data with IsoplotR (Vermeesch, 2018), results are also available as supplementary material.

We use the $X_{Ce^{4+}}^{melt}/X_{Ce^{3+}}^{melt}$ index (Smythe and Brenan, 2016), to constrain the fO_2 of the magmas from central TMP (equations 1 and 2). Most zircon based oxybarometers available in the bibliography (Ballard et al., 2002; Chelle-Michou et al., 2014; Smythe and Brenan, 2016; Trail et al., 2012) rely on the lattice strain model (Blundy and Wood, 1994) and are strongly influenced by the LREE content of zircon. The lattice strain model satisfactorily explains the behavior and HREE, but LREE, on the other hand, commonly deviates from the model predictions, compromising the robustness of most oxy-barometers. As demonstrated by Zou et al. (2019), Smythe and Brenan's $X_{Ce^{4+}}^{melt}/X_{Ce^{3+}}^{melt}$ index might be considered as REE independent and magmatic fO_2 is estimated with basis on the temperature of the magmas (Ti-in-zircon thermometer from Ferry and Watson (2007), assuming SiO₂ and TiO₂ activities of 1.0 and 0.65 respectively), non-bridging oxygens (NBO, Virgo et al., 1980) and mole

fraction of water (estimated with the hygrometer from Waters and Lange, 2015) as it follows:

1)
$$\frac{x_{Ce^{4+}}^{melt}}{x_{Ce^{3+}}^{melt}} = \left[\frac{\sum Ce_{zircon} - \left(\sum Ce_{melt} * D_{Ce^{3+}}^{zircon/melt}\right)}{\left(\sum Ce_{melt} * D_{Ce^{4+}}^{zircon/melt}\right) - \sum Ce_{zircon}}\right] * 1.04877;$$
2)
$$ln\left[\frac{x_{Ce^{4+}}^{melt}}{x_{Ce^{3+}}^{melt}}\right] = \frac{1}{4} \ln f O_2 + \frac{13136(\pm 591)}{T} - 2.064(\pm 0.011) \cdot \frac{NBO}{T} - 8.878(\pm 0.112) \cdot xH_2O - 8.955(\pm 0.091)$$

3.4. Results

3.4.1. Whole-Rock Geochemistry

In this section we directly compare whole-rock geochemistry analyses from the different TMP deposits. As a first selection criteria and in view of the thick weathering profile at the Amazonian region, the whole-rock geochemical data were plotted on the MFW diagram after Ohta and Arai (2007) (Fig. 3). The diagram was idealized with basis on a dataset of igneous rocks and their respective weathered products, where principal component analysis allows the M and F vertices to capture mafic to felsic differentiation sequence, whereas the W apex relates with the degree of weathering. Accordingly, the samples that plot on the center of the diagram and scatter towards the W vertice likely present some degree of weathering that might disturb their original geochemical signature and, consequently, these samples were excluded from the database.



Fig. 3. FMW ternary diagram after Ohta and Arai (2007) for the whole-rock geochemistry database. Samples that plot on the shaded area indicate higher degree of weathering and were not considered for the results and discussion sections.

3.4.1.1. Classification Diagrams

With respect to their geochemical classification, the most prominent difference between the older and younger igneous suites is the much wider compositional range covered by the former, in particular for the intrusive sequence (Fig. 4a). The Tocantinzinho, São Jorge and Patrocínio deposit rocks show a significant variation on the diagram and vary between diorites, monzonites, quartz-monzonite, granodiorites, tonalites and granites. The later also shows lower silica syenites, quartz-syenites and monzodiorites. The Chapéu do Sol rocks show a smaller variation and plot on the quartz-syenite, granite and alkali-granite fields. Equivalent compositions are verified for the Coringa deposit, with the extrusive sequence essentially rhyolitic or alkalirhyolitic.



Fig. 4. De la Roche et al. (1980) classification diagram for the OMS (a), with coeval volcanics from the Coringa deposit at the top-left. (b) Classification diagram for the YMS with the V3 volcanics plotted at the smaller top-left diagram.

The intrusive sequence of YMS (Palito, São Jorge and Batalha deposits) shows a much narrower geochemical variation (Fig. 4b). The three deposits host rocks vary between granite and alkali-granite with a single granodiorite sample for the Batallha deposit. The V3 deposit is hosted by a volcanic sequence that is dominated by rhyolites, dacites, lati-andesites and, more rarely, quartz-trachyte.

The diagrams from Figure 5 brings SiO₂ vs. Fe-index, SiO₂ vs. MALI and an A-B plot for constraining the sample's aluminosity (Frost et al., 2001; Villaseca et al., 1998). In this study we gave preference to use Villaseca's A-B diagram instead of the classic A/CNK vs. A/NK plot (Shand, 1943). The former brings aluminosity as a function of maficity, hence petrologic trends are more promptly identified. In general, OMS deposit rocks might be separated into three categories: group I comprises ferroan (Fig. 5a), calc-alkalic (Fig. 5b) and preferentially peraluminous granites (s.l.) described in the Patrocínio and Tocantinzinho deposits (Fig. 5c); group II is defined by magnesian to ferroan, alkali-calcic to calc-akalic, metaluminous to felsic peraluminous rocks from the Tocantinzinho, São Jorge, Chapéu do Sol and Patrocínio deposits; and group III is characterized by ferroan, alkalic and metaluminous to low-peraluminous granitoids found in the Patrocínio, Tocantinzinho, Coringa and São Jorge deposits.





Fig. 5. Frost's classification diagrams for OMS and YMS, with $SiO_2 vs.$ Fe-index (a), $SiO_2 vs.$ MALI (b), and A-B diagram after Villaseca et al. (1998) (c), where A = AI - (K + Na + 2Ca) and B = Fe + Mg + Ti, calculated for millications. Extrusive rocks from the Coringa and V3 deposits are plotted for comparison purposes. Groups I, II and III rocks from OMS are pinpointed on the smaller diagrams.

Within the YMS, the Palito and Batalha samples are ferroan, alkali-calcic and metaluminous to moderately-peraluminous. On the A-B diagram, the Batalha granitoids do not define any noticeable trend and instead, samples cluster around the same value of maficity (at approximately B = 40) and spread towards the low-peraluminous and moderately-peraluminous fields. The V3 volcanics resemble the trend identified for the OMS, with magnesian intermediate samples and ferroan acid members that vary from alkalic to calc-alkalic and define a clear negative slope on the A-B diagram from metaluminous to felsic-peraluminous.

3.4.1.2. Major-element contents

As previously mentioned, the São Jorge and the Chapéu do Sol deposits are associated with both magmatic sequences, however, due to the lack of younger samples, our models for both deposits will concern only OMS. Harker diagrams for the OMS show that intermediate samples tend to scatter more strongly than the acid members and, for silica values over 65%, the trend is linear. Geochemical modelling shows that fractional crystallization accounts for the geochemical variability within OMS, which is characterized by three main petrologic trends. Within the higher silica side (SiO₂ > 65 wt. %), one of trends accounts for part of the Patrocínio and Tocantinzinho samples (group I granites). It starts from a granodioritic melt that fractionates plagioclase, pyroxene, biotite, magnetite and titanite, with a monzodiorite cumulate (green array in Figure 6). The other silica richer trend (group II rocks) is characterized by a tonalitic initial composition and involves fractionation of albitic plagioclase, amphibole, biotite, magnetite and titanite (red array in Fig. 6), and is also compatible with a monzo-diorite cumulate. This trend encompasses most of the OMS, including the Tocantinzinho, Coringa, Chapéu do Sol, São Jorge (older) granite and part of the Patrocínio samples. The lower silica spectrum, or group III rocks, involves syenites and monzonites from the Patrocínio deposit and a few Tocantinzinho, and Coringa samples that evolved through fractionation of K-feldspar, plagioclase, biotite, apatite, clinopyroxene and ilmenite (gray array in Fig. 6).



Fig. 6. Silica vs. major oxides diagrams for OMS rocks (symbols are the same as in the previous figures). Red, green and gray arrays mark the petrologic trends modeled with the respective minerals involved. The accuracy of the models is given by the R² parameter, which is defined by the sum of the differences between the theoretical and real differentiated melts for each element squared. Abbreviations: Am (amphibole), PI (plagioclase), Bt (biotite), Px (pyroxene), Mag (magnetite), Ttn (titanite), Ap (apatite), Ilm (ilmenite).

Samples from the YMS, particularly the intermediate rocks, scatter more strongly than the OMS on the Harker diagrams (Fig. 7). Three trends accounts for the petrologic evolution of the YMS. Intermediate V3 volcanics show an evolution coherent with a lati-andesite initial liquid that fractionates K-feldspar, amphibole, anorthitic-plagioclase and biotite (yellow array in Fig. 7) and generates a quartz-latite liquid and a diorite cumulate.

The acid members of the V3 deposit define a trend compatible with a rhyolitic initial composition that differentiates to alkali-rhyolite through fractionation of albitic-plagioclase, K-feldspar, pyroxene and titanite, with a syenite cumulate (yellow array in Fig. 7). A relatively similar trend comprises the Batalha and Palito granitoids (black array in Fig. 7). This evolution starts from a granitic composition and is consistent with extraction of albitic-plagioclase (44%), K-feldspar (42%), pyroxene (7%), titanite (3%) and apatite (4%), generating an alkali-granitic liquid and a syenite cumulate.



Fig. 7. Silica vs. major oxides for YMS rocks. Yellow and black arrays mark the petrologic trends modeled, with the minerals involved and the R² parameter indicated at the top. Symbols are the same as in the previous figures. Abbreviations: Kfs (K-feldspar), Am (amphibole), Pl (plagioclase), Bt (biotite), Px (pyroxene), Mag (magnetite), Ttn (titanite).

3.4.1.3. Trace Element Contents

REE spidergrams reveal similar patterns for OMS samples, characterized by a moderate level of HREE depletion (average La/Yb_N \geq 12.1, Figs. 8a – 8e). The steepest pattern was identified for the São Jorge deposit, in both older and younger granites (Fig. 8a) with averages La/Yb_N of 35.4 and 81.5 respectively that are accompanied by positive to mildly negative Eu anomalies. The Patrocínio samples (Fig. 8b) also define a steep slope, yet more subtle than the older São Jorge granite, and are accompanied by null or moderately negative Eu anomalies. The Chapéu do Sol, Coringa and Tocantinzinho deposits (Figs. 8c – 8e) are characterized by less fractionated trends (average (La/Yb)_N ratios of 19.5, 18.8 and 12.1 respectively) and slight to moderately negative Eu anomalies.

REE spidergrams for the YMS (Figs. 8f – 8h) show a much more subtle fractionation between light and HREE when compared with the older sequence (except for the younger São Jorge granite, Fig. 8a). The Eu anomalies are more restrict and vary from moderately negative to strongly positive. The V3 volcanic rocks show a moderate degree of fractionation (Fig. 8f, with average (La/Yb)_N of 17.4) and moderately negative to negligible Eu anomalies. The Palito and Batalha deposit rocks behave similarly (Figs. 8g and 8h, average (La/Yb)_N ratios of 10.9 and 8.1 respectively) and define smoother trends towards lower HREE contents, with moderate to strongly negative Eu anomalies. The trace-element spidergram (Fig. 8i) shows that YMS is slightly enriched in HFSE (Ti, Dy, Y, Zr, Sm) and show lower Sr contents.

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Fig. 8. Chondrite normalized (Boynton, 1984) REE spidergrams for the OMS (a – e), YMS (f – h) and trace-element spidergrams normalized by the primitive mantle (Sun and McDonough, 1989) for both sequences. The respective colored fields represent the entire range covered by each deposit/unit. Eu anomaly calculated as $Eu/Eu^* = Eu_N/\sqrt{(SmN. GdN)}$.

Figure 9 shows trace-element ratios plotted against maficity (Fe + Ti + Mg calculated for millications) or Eu anomaly calculated as Eu_N/Eu^* ($Eu_N = concentration$ of Eu normalized by the chondrite after Boynton (1984); $Eu^* = \sqrt{Sm_N.Gd_N}$). On the Dy/Yb vs. maficity plot for the older sequence (Fig. 9a) it's clear that the older São Jorge granite is the unit with the largest range of Dy/Yb, and is followed by the Tocantinzinho and Chapéu do Sol samples that show a minor spread between $1 \leq Dy/Yb \leq 2$.





Fig. 9. Maficity vs. Dy/Yb (a), Eu/Eu* vs. Sr/Y (b) and Eu/Eu* vs. La/Yb (c) plots for OMS and YMS. Dy/Yb ratio is strongly influenced by amphibole as the mineral shows high Kd's for both elements. Sr/Y and La/Yb might also be influenced by amphibole, however, plagioclase and pyroxene on a lesser extent might also shift the ratios towards higher or lower values.

The Patrocínio and Coringa samples don't vary significantly and show Dy/Yb ratio around 2. The younger sequence shows a similar trend and spread horizontally on the plot, with maficity values between 10 and 200 for a Dy/Yb ratio around 2. The younger São Jorge granite stands as an outlier and shows Dy/Yb ratio from 2 to 4. The Sr/Y vs. Eu_N/Eu^* diagram (Fig. 9b) shows a positive correlation between the two parameters. In general terms, the Patrocínio, Coringa, São Jorge and Chapéu do Sol show predominantly moderate Sr/Y values that fall between 5 and 50. The only sample cluster was identified for the Tocantinzinho deposit, that shows predominantly low ratio (Sr/Y \leq 5), with scarce exceptions. A similar behavior was identified for the younger São Jorge granite samples show moderate to high ratios (Sr/Y \geq 50) followed by null or positive Eu anomalies.

Both older and younger igneous sequences can be separated into low, moderate and rarer high La/Yb rocks. On average, the La/Yb and Eu_N/Eu* correlate positively. For the OMS, Figure 9c shows that the São Jorge samples vary from moderate to high ratios ($30 \le La/Yb \le 100$). The Coringa, Patrocínio and Chapéu do Sol samples show predominantly moderate values ($20 \le La/Yb \le 50$), whereas the Tocantinzinho deposit shows mainly low La/Yb rocks (≤ 20). For the younger sequence, the São Jorge granite shows the highest La/Yb ratios (> 100), which is accompanied by the highest Eu_N/Eu*. Moderate values ($20 \le La/Yb \le 50$) were acquired for the V3 volcanic units, whereas the Batalha and Palito granitoids show the lowest ratios (La/Yb ≤ 20).

In summary, OMS shows a wide compositional range and rocks vary from magnesian to slightly ferroan, alkali-calcic to calc-alkalic, metaluminous to moderately peraluminous and show steep REE patterns. Three trends accounts for the OMS evolution: a magnetite and pyroxene bearing one involving granodiorites and granites; an amphibole and magnetite one that comprises most OMS-hosted deposits; and a third one involving pyroxene and ilmenite fractionation on K-rich magmas. YMS shows similar MALI and aluminosity, however with a more restrict compositional range and more subtle REE patterns on essentially ferroan samples (excepted for intermediate V3). Our models show that these rocks evolved on an reduced and predominantly anhydrous trend.

3.4.2. Zircon geochemistry

3.4.2.1. Morphology and textural description

At this study we present three new geochronology results from samples collected at central TMP and reexamine two samples (USP14-136 and USP14-160) presented by Cassini et al. (2020) for inheritance. Sample USP14-160 (granodiorite) is characterized by subhedral grains, with rounded or partially corroded edges, 2:1 elongation ratio, with predominantly oscillatory but also broad and patchy zonings. Round shaped xenocrystic cores displaying both dissolution and resorption textures

are also common (Fig. 10a). Sample USP14-144 (granodioritic porphyry) is dominated by euhedral to subhedral, elongated grains (between 2:1 and 3:1), with oscillatory and less frequent patchy and sector zonings. Two types of cores are observed on this sample: one comprises rounded, partially resorbed xenocrystic cores (Fig. 10b),





Fig. 10. Cathodoluminescence images from selected zircon grains and the respective concordia-discordia diagrams from the samples analyzed in this study. Spots are 20 μ m wide. 1-3, 10, 11, 17-19 (partially dissolved) and 30-32 show inherited xenocrystic cores (grain 32 is partially resorbed); 4, 5, 14, 20, 25, 26 and 35 show oscillatory zoning; 6 and 7 are broad zoned grains; 8, 9, 15 and 27 show patchy zoned zircon grains; 12, 13, 33 and 34 show autocrystic cores; 16, 22, 23, 28, 29, 36 and 37 show sector zoning; 21 and 24 are homogeneous zoned.

commonly fractured and metamictic; and the other, comparatively more frequent, is characterized by oscillatory or homogenously zoned nuclei and lacks dissolution or resorption textures. Sample USP14-83, an aplite dyke of syenitic composition (R1-R2 classification), comprises euhedral and subhedral zircon grains, with 2:1 elongation and well preserved oscillatory zoning (Fig. 10c). Round-shaped, partially resorbed xenocrystic cores with homogeneous, patchy or sector zonings are also observed. Sample USP14-91 represent a coarser-grained syenite and is characterized by subhedral to anhedral grains, with elongation that varies between 1:1 and 2:1 (rarer 3:1 grains), predominance of oscillatory zoning with minor examples of sector and patchy zonings. Cores show predominantly oscillatory and, less frequently, homogenous zonings with rarer xenocrystic and metamictic domains (Fig. 10d). Sample USP14-136 (monzonite) is composed by euhedral to subhedral grains, with elongation between 2:1 and 3:1, with well preserved oscillatory and sector zonings. A detailed evaluation and description of the grains allowed the identification of two types of cores: rounded xenocrystic cores that commonly display dissolution textures and zoning patterns that truncates the rim (Fig. 10e); and comparatively homogenous rounded cores that show concordant zoning patterns.

3.4.2.2. U-Pb Dating (LA-ICP-MS)

The granodiorite sample (USP14-160) presents a continuous distribution of 207 Pb/ 206 Pb ages between 2000 and 2100 Ma, as demonstrated by the frequency histograms from Figure 10a, with a more pronounced peak at ca. 2020 Ma. Autocrystic cores were evaluated and yielded concordant ages of 2031.2 ± 2.0 Ma (n = 15), whereas 6 xenocrystic cores revealed ages higher than 2050 Ma. Rims analyses yielded 2011.7 ± 4.5 Ma (n = 13) understood as the sample's magmatic age.

The granodioritic porphyry (USP14-144) presents 207 Pb/ 206 Pb ages that spread from 1800 to 2040 Ma, with a more pronounced peak at ca. 1980 Ma (Fig. 10b). Five xenocrystic cores were analyzed and yielded concordant results that converge to 2010.9 ± 8.1 Ma. Autocrystic cores and rims point to similar ages, and 22 grains align

on a discordia with upper intercept at 1986.9 \pm 5.9 Ma, considered as the samples magmatic age.

For the aplitic syenite sample (USP14-83) 207 Pb/ 206 Pb age histograms (Fig. 10c) shows that results concentrate at ca. 1990 Ma, with minor older and younger examples. A total of 15 xenocrystic cores were evaluated and defined a discordia with upper intercept at 2012.7 ± 6.7 Ma. Core and rim analyses yielded discordant results and 16 grains align on a discordia with upper intercept at 1987.3 ± 7.1 Ma, interpreted as the magmatic age.

The syenite sample (USP14-91) also shows 207 Pb/ 206 Pb ages clustered at ca. 1990 Ma (Fig. 10d). Cores and rims analyses converge to a concordia age of 1993.7 ± 2.7 Ma (n = 11). Xenocrystic cores are rare in this sample and were not evaluated.

The monzonite sample (USP14-136) shows 207 Pb/ 206 Pb ages that spread between 1900 and 2060 Ma, with a clear cluster at ca. 1980 Ma (Fig. 10e). Twelve xenocrystic cores were analyzed and yielded discordant ages that roughly align on a discordia with upper intercept at 2055.5 ± 8.7 Ma. Cores and rims analyses revealed 18 grains that converge to a concordia age of 1974.6 ± 1.9 Ma, understood as its magmatic age.

3.4.2.3. Trace element contents

Zircon Eu anomalies are constrained on the diagram from Figure 11a, where Eu/Eu* is plotted against Zr/Hf (as a proxy for differentiation). At a first glance, all samples show predominantly Eu/Eu* < 0.5, with a few exceptions for USP14-136, 144 and 160. Accordingly, samples USP14-91 and 144 cover a similar range and Eu/Eu* varies from 0.1 to 0.5, with a few values closer to unity or higher. Sample USP14-136 defines a gentle negative trend on the diagram, with core Eu/Eu* between 0.1 and 0.5, and 0.25 to 0.7 for the rims, with minor values greater than 1. USP14-83 also defines a subtle negative trend, with Eu/Eu* varying from 0.25 on the cores to 0.5 on the rims as Zr/Hf decreases. Grains from sample USP14-160 scatter on the plot and Eu/Eu* ratio

varies from 0.1 to 2.0, without any noticeable trend. The most prominent feature regards the higher Zr/Hf ratio acquired for zircon cores.

The Th/U vs. Dy/Yb plot marks how the zircon grains from all samples evolved regarding middle- and HREE fractionation and, accordingly, all samples define a positive trend (Fig. 11b) and zircon cores show higher Dy/Yb and Th/U than the rims. Sample USP14-83, despite having the most scattered pattern, shows the highest values for both ratios and grains plot on the upper right part of the graph (Dy/Yb varies from 0.4 to 1.0 and Th/U from 0.5 to 10). Samples USP14- 91 and 144 distribute similarly and Dy/Yb varies from 0.4 on the cores to 0.2 on the rims as Th/U falls from 1.2 to 0.4 (steeper pattern for USP14-144). Samples USP14-136 and 160 define sub parallel trends, the later characterized by lower Th/U ratios as Dy/Yb decreases from 0.4 on the cores to 0.2 on the rims.

The plot from Figure 11c shows the LREE-index (LREE-I = Dy/Nd + Dy/Sm), as proposed by Bell et al. (2016), plotted against Ti. The parameters correlate negatively and, for LREE-I values greater than 20, the trend shows a clearer linearity. Roughly all grains from sample USP14-83, and significant proportion of samples USP14-160, 144 and 136 plots on the scattered part of the graph (LREE-I < 20). Zircon grains from sample USP14-91, on the other hand, behave more linearly and plot predominantly on the right side of the graph (LREE-I > 20).





Fig. 11. Zircon geochemistry with Zr/Hf vs. Eu/Eu* (a) and Th/U vs. Dy/Yb plots (b), where both Zr/Hf and Th/U ratios were used as proxies for differentiation. Bottom right smaller graph in (b) shows the polynomial regressions with the general trend for each sample. (c) Light REE index (LREE-i) as proposed by Bell et al. (2016) vs. Ti plot. The index is calculated as LREE-i = (Dy/Nd + Dy/Sm), in order to constrain the proportion between middle and light-REE in zircon grains. Grains with low LREE-i show high LREE content, which might indicate hydrothermal alteration (or LREE rich inclusions such as apatite or monazite on the ablated spot).

3.4.2.4. Ti-in-zircon thermometry

The Ti-in-zircon (TZirc.Ti) thermometer after Ferry and Watson (2007) was applied to constrain magmatic temperatures and the results are summarized on Table 3 (values below 620°C and above 970°C were discarded and not considered on our database). The plot from Figure 12a shows how TZirc.Ti and zircon saturation temperature (TZirc.Sat) (Watson and Harrison, 1983) relate for each sample/grain analyzed and, accordingly, results distribute in three fields: i) upper part of the plot where TZirc.Ti > TZirc.Sat +100, hence zircon-undersaturated field; ii) shaded area between 1:1 and 1:100 ; and iii) bottom part of the plot with TZirc.Ti < TZirc.Sat, zirconoversaturated field. Whereas autocrystic zircons will plot on the bottom and eventually on field ii, inherited grains (ante- and xenocrysts) spread through all fields.

Table 3

Summary of zircon saturation temperature (T.Zirc.Sat), Ti-in-zircon thermometer (T.Zirc.Ti) and magmatic fO_2 values acquired for OMS.

Samples	T.Zirc.Sat ⁽¹⁾	T.Zirc.Ti ⁽²⁾ (°C)				$\log fO_2^{(3)}$					
	(°C)	Min	Q1	Q2	Q3	Max	Min	Q1	Q2	Q3	Max
USP14-160	798	674	717	734	783	818	-20.9	-18.1	-17.1	-15.6	-14.4
USP14-144	794	715	749	760	767	796	-16.2	-15.9	-15.1	-13.9	-12.2
USP14-83	754	705	762	794	813	864	-13.4	-12.0	-10.8	-9.5	-5.1
USP14-91	793	700	732	767	775	787	-17.3	-16.3	-15.2	-14.7	-14.0
USP14-136	819	725	763	787	807	820	-16.9	-15.6	-15.1	-14.3	-13.5

 Watson and Harrison (1983); (2) Ferry and Watson (2007), absolute error of ±30°C; (3) Smythe and Brenan (2016), propagated uncertainty of ±1.2 log units.

Samples USP14-144 and 160 show the lowest magmatic temperatures (medians of 768 °C and 782 °C respectively) with a broader distribution for the later, and are characterized by intermediate TZirc.Sat (794 °C and 798 °C respectively). Zircon grains distribute between fields ii and iii, with greater concentrations for the TZirc.Ti < TZirc.Sat field. Samples USP14-91, 136 and 83 show progressively higher magmatic temperatures, and median TZirc.Ti are respectively 786 °C, 811 °C and 818 °C. The first

two show grains that equally distributed between fields ii and iii, with intermediate and high TZirc.Sat (793 °C and 819 °C respectively). Sample USP14-83 differs from the others and its zircon grains distribute essentially on fields i and ii, and are accompanied by the lowest TZirc.Sat (754 °C).

3.4.2.5. Magmatic *f*O₂ estimates

In order to make the data easier to read and comparable with other paper's datasets, we treat magmatic fO_2 in log units above or below the fayalite-magnetitequartz (FMQ) oxygen buffer (results are summarized on Table 3). The graph from Figure 12b shows magmatic temperature (TZirc.Ti) plotted against Δ FMQ (xenocrysts, high La and low LREE-i zircon grains were ruled out). Sample USP14-83 shows the highest fO_2 values and zircon grains plot on the top part of the graph (values higher than Δ FMQ + 4). However, these results should be treated cautiously, as the sample shows predominantly low LREE-i zircon grains.





Fig. 12. Zircon saturation temperature (Watson and Harrison 1983) vs. Ti-in-zircon temperature (Ferry and Watson 2007) plot. The plot separates fields where zircon saturation is not achieved by the hosting magmas (top of the diagram) and, conversely, fields where zircon might be extracted from the magmas (center and bottom parts). Inherited grains might plot in all fields, whereas autocrystic grains will plot on the center and bottom parts. (b) Magmatic fO_2 treated as log units above or below the fayalite-magnetite-quartz oxygen buffer plotted against magmatic temperature (T Zirc.Ti).

The granodioritic porphyry (sample USP14-144) shows the second highest fO_2 values, with Δ FMQ from 0 to + 4. Samples USP14-91 and 136 cover a similar and narrower fO_2 range, with Δ FMQ between 0 and + 1. Sample USP14-160 is characterized by the widest fO_2 range and samples tend to scatter more strongly (Δ FMQ varies from - 4 to 0).

3.5. Discussion

3.5.1. A petrogenesis perspective: generating the older and younger magmatic sequences

In the Tapajós Mineral Province, a clear feature of the OMS (igneous suites of 2.00 – 1.95 Ga) is its wider compositional range when compared with the YMS (igneous suites of 1.90 – 1.86 Ga, Figs. 4a and 4b). Yet, an interesting and relevant common ground for both magmatic sequences is the presence of metaluminous samples with higher maficity values (with exception of the Batalha granitoids as shown in Fig. 5c). The balance between Al and Na, Ca and K is particularly important in granitic rocks geochemistry as it efficiently constrains their petrogenesis (Clemens et al., 2011; Clemens and Stevens, 2012; Frost et al., 2001; Frost and Frost, 2013, 2011; Moyen et al., 2017; Villaseca et al., 1998) and, as such, it indicates metaluminous mafic sources for both OMS and YMS. Differences between the magmatic sequences are better evidenced on the Fe-index and MALI vs. silica diagrams (Figs. 5a and 5b) and major-oxides plots (Figs. 6 and 7), which suggests contrasting melting conditions and magmatic evolution, in spite of similar sources.

OMS rocks might be divided into three categories. Group i granitoids correlates with the Cuiú-Cuiú Complex, are found on the Patrocínio and Tocantinzinho deposits (southern and central TMP respectively), show slightly higher silica contents, are peraluminous, magnesian to ferroan, calc-alkalic to calcic and comprises granites and granodiorites compatible with mafic and oxidizing sources, with moderate to strong continental crust contribution. The group comprises the oldest granodiorite (sample USP14-160) dated in this contribution at 2011 Ma, characterized by a magnetite bearing and amphibole-free evolution (green array in Fig. 6) generating the horizontal distribution of samples on the Dy/Yb plot the moderate to low Sr/Y and La/Yb ratios (Fig. 9). These rocks represent the first batches of magmatism upon the onset of subduction on the TMP at ca. 2.0 Ga, that according to Cassini et al. (2020) is characterized by a strong crustal component due to incorporation of trench derived sediments and/or subcrustal-erosion of the subducted plate (ϵ Nd_(T) of -8.36 acquired by the authors).

Group ii granitites (s.l.) predominates at the TMP as a whole and correlates with the Creporizão Intrusive Suite. It comprises samples from the Tocantinzinho, São Jorge (older granite) and Chapéu do Sol gold deposits (northern and central TMP), with a few examples from the Patrocínio deposit (sample USP14-144 dated at 1986 Ma). The rocks are metaluminous to mildly peraluminous, magnesian to slightly ferroan, calc-alkalic to alkali-calcic and suggest mafic to intermediate, oxidizing sources typical of subduction-related, I-type granites. Geochemical modelling demonstrates fractional crystallization as the main differentiation mechanism and a hydrous and oxidized trend consistent with plagioclase, amphibole, biotite, magnetite and titanite (red array in Fig. 6). Middle-REE depletion (clearer for the Tocantinzinho samples, Fig. 8) and the distribution on the Dy/Yb, Sr/Y and La/Yb plots (Fig. 9) reinforce the role of amphibole. Samples from the Coringa deposit (southern TMP) plot on the magnesian-ferroan transition and are predominantly alkalic, compatible with highly differentiated I-type granites (Frost et al., 2001; Frost and Frost, 2011). In addition, these samples cover the higher silica spectrum of group ii's trend (red array in Fig. 6), suggesting a similar petrologic evolution. Considering the more discrete variation on the Dy/Yb, Sr/Y and La/Yb ratios, amphibole most likely played a lesser role on the evolution of the Coringa rocks. As a whole, group ii rocks might be might be understood as differentiated, I-type granites that represent the evolution of the arc-magmatism.

Group iii comprises lower silica, K-rich ($K_2O > 5$ wt.%), metaluminous to peraluminous, ferroan and alkalic syenites (quartz-syenites) and monzonites with ages between 1974 and 1993 Ma. Major and trace element patterns show that group iii derives from anhydrous, metasomatized, mafic and reducing parental magmas with restrict crustal contribution ($\epsilon Nd_{(T)}$ from -1.64 to +1.69 acquired by Cassini et al., 2020). The authors also demonstrated how these rocks evolved on an anhydrous and reduced petrologic trend (pyroxene and ilmenite bearing) as a consequence of corner flow induced, decompression mantle melting. Early extraction of plagioclase is symptomatic of anhydrous melts and explains the Eu anomalies (negative), Sr and Ba depletions, and low Sr/Y and La/Yb ratios. This group of rocks, that accounts for about 15% of our database and encompasses Patrocínio, Tocantinzinho, Coringa and São Jorge samples, is not constrained on the S-I-M-A classification (Chappell and White, 2001) and it is often treated as K-rich calc-alkaline granitoids (Bonin, 2004, 1990; Bonin et al., 2020) or as Fe-K granitoids (Laurent et al., 2014) that are typical of post-orogenic or collisional tectonic settings (Bonin, 2004; Frost et al., 2001; Liégeois et al., 1998). Despite their abundance in Proterozoic terrains throughout the world (Bogaerts et al., 2006; Ferré et al., 1998; Ferreira et al., 1998; Kouankap Nono et al., 2010; Laurent et al., 2014; Vander Auwera et al., 2011), the precise petrogenetic mechanism behind high-K, metaluminous and ferroan granitoids is still debatable.

Within the YMS, V3 volcanics (Iriri Group) vary from metaluminous to peraluminous, alkalic to calc-alkalic and are magnesian on the lower silica side and ferroan on the more acid members, geochemical attributes that suggest oxidizing to reducing mafic parental magmas with contribution of preexisting crust. Geochemical modelling indicates that intermediate V3 (and the few younger São Jorge granite samples) evolved through K-feldspar, amphibole, anorthite-rich plagioclase and biotite extraction (yellow array in Fig. 7), yielding higher Dy/Yb, Sr/Y and La/Yb ratios (Fig. 9). More prominent differences between the older and younger sequences are evidenced by the acid V3 volcanics and by the Palito and Batalha granitoids (that correlate with the Parauari Intrusive Suite). The rocks show similar aluminosity with the OMS but are alkali-calcic, essentially ferroan, show a much narrower compositional range and evolved on a pyroxene and magnetite-free trend (black array in Fig. 7), characterized by lower Sr/Y, La/Yb and Eu/Eu* ratios. These geochemical attributes mark a transition from hydrous and oxidizing, to anhydrous and reducing mafic sources.

As a whole, OMS and YMS show subtle geochemical differences and contrasting petrologic trends and these differences lend support to a changing tectonic framework on the TMP at ca. 1.88 Ga, from a magmatic-arc context to a post-orogenic or collisional setting (Juliani et al., 2005; Lamarão et al., 2005, 2002; Santos et al., 2004, 2001, 2000). The suppression of subduction and the absence (or low activity) of slab-derived fluids positions SCLM as the main magmatic source and explains the higher HFSE content of YMS.
3.5.2. Insights from zircon geochemistry: examples from the Patrocínio gold mineralization

Whole-rock geochemistry shows that the OMS might be grouped into three categories: group i involves higher-silica granites and granodiorites that evolved on a dryer trend through fractionation of pyroxene, magnetite and titanite; group ii involves granites (s.l.) and are compatible with extraction of amphibole, magnetite and titanite; and group iii accounts for the low-silica, high-K syenites and monzonites that evolved on a pyroxene- and ilmenite-bearing trend. Zircon textural description and geochemical analyses for groups I, ii and iii reveal a protracted petrologic history of approximately 40 Ma.

Sample USP14-160 (granodiorite) belongs to group i, shows the oldest age among the rocks dated in this study (2011 Ma), autocrystic cores of 2031 Ma and xenocrystic cores of 2052 Ma, both characterized by higher Zr/Hf and Th/U than the rims (Figs. 10a, 11a and 11b). The abundance of inherited cores combined with the whole-rock $\epsilon Nd_{(T)} = -8.36$ (Cassini et al., 2020) and the high TZirc.Sat (798 °C) supports the contribution of preexisting crust for the formation of group i magmas. A few grains stand as exceptions and show Hf-enriched cores, reflecting episodic injections of new magma batches as zircon crystallize. Partially corroded and rounded edges and the low whole-rock Zr content of this sample (179.6 ppm) suggest early zircon extraction. According to our models, this sample belongs to a magmatic series that evolved through profound extraction of plagioclase (~71% of the cumulate composition), and a strong negative Eu anomaly would be ubiquitous on the evolving melt. Loader et al. (2017) demonstrated how titanite fractionation might potentially drive the melt towards positive (or only subtly negative) Eu anomalies, as the mineral incorporates preferentially the other trivalent REE ($Kd_{titanite}^{REE 3+} > 100$, Bachmann et al., 2005). Hence, the chemical effects of plagioclase extraction in group i granites is apparently counterbalanced by synchronous extraction of titanite (and less importantly pyroxene), which assigns the evolving magma and subsequently crystallizing zircon grains (or rims) their $Eu/Eu^* \ge 0.5$ and lower Dy/Yb ratios (Figs. 11a and 11b). Additionally, the preferential incorporation of Th by titanite explains the evolution

towards lower Th/U (Harrison et al., 2007a; Lee et al., 2020). Despite the compatibility with magnetite, the plot from Figure 12b shows fO_2 values close to or a few log units below the FMQ buffer, just enough to stabilize the mineral.

The granodioritic porphyry (sample USP14-144) belongs to group ii granitoids and is characterized by magnetite, titanite and amphibole fractionation, a magmatic age of 1986 Ma and rounded, partially corroded inherited xenocrystic cores dated at 2010 Ma (Fig. 10b), compatible with group i ages. Zircon morphology (3:1 elongation) and the synchronicity of core and rims suggest a rapid crystallization history for this sample, which is compatible with the shallower crustal level expected for a porphyry intrusion. Profound extraction of plagioclase (~73% of the cumulate) explains the evolution towards lower Eu/Eu* as Zr/Hf decreases and, the few samples with higher Eu/Eu* likely reflects competing titanite extraction. However, differently than sample's USP14-160 case, titanite is approximately 4 times rarer within group ii's petrologic trend, fact that diminishes significantly its geochemical effects on the evolving melt. Combined fractionation of titanite and amphibole modeled for group ii yields the steepest array on the Th/U vs Dy/Yb plot and the lowest magmatic temperature (768 °C) acquired in this study. In addition, the oxidizing condition of this sample is sustained by geochemical modelling and by fO_2 values between $\Delta FMQ + 0$ and $\Delta FMQ +$ 4.

Samples USP14-83, 136 and 91 (quartz-syenites and quartz-monzonites) belong to the high-K series (group iii) that is characterized by a dry, reduced and protracted magmatic history. USP14-91 marks the onset of the high-K magmatism at ca. 1993 Ma (Fig. 10c). This sample presents low silica contents (~60 wt.%) and zircon stabilization is likely due to the high whole-rock Zr (357.7 ppm) (Fig. 12a indicates the predominance of autocrystic grains). Sample USP14-136 shares similar characteristics, yet, much younger magmatic age (1974 Ma, Fig. 10d), representing a late stage pulse of the high-K magmatism. Inherited zircon grains dated at 2055 Ma reflects a longer period of residence on deeper hot zones by these primary magmas (Annen et al., 2006), adequately explaining the positive to slightly negative ɛNd_(T) acquired for group iii rocks (Cassini et al., 2020). Sample USP14-83 intrudes as synmagmatic aplitic dykes and

represents the evolution of the high-K magmatism. Its low whole-rock Zr content (127.4 ppm) suggests that the magma underwent previous zircon extraction and, consequently, the 1987 Ma age (Fig. 10e) should be understood as inherited (Fig. 12a indicates the predominance of antecrystic zircon grains). This idea is supported by the incompatibility between our geochemical modelling results (that indicates a reduced petrologic trend) and the extreme high fO_2 values acquired for group iii (Fig. 12b). The LREE index vs. Ti plot (Fig. 11c) indicates that USP14-83 and 136 in a lesser extent, are anomalously LREE enriched, reflecting either hydrothermal alteration or mineral inclusions on the ablated spot (Bell et al., 2019, 2016), which might compromise the reliability of the results. As a consequence, zircon trace-element contents for these rocks should be looked at cautiously. The Eu/Eu* values predominantly below 0.5 denies fractionation of titanite and the smoother drop on the Dy/Yb ratio as Th/U decreases negates amphibole extraction, supporting the dry, ilmenite- and pyroxenebearing evolution modeled for group iii. Its reducing affinity, as pinpointed by geochemical modeling, is also supported by the fO_2 values below ΔFMQ +1. Additionally, the higher magmatic temperatures acquired for group iii syenites and monzonites (786° to 811° C) attest the dry characteristic of the high-K magmatism.

3.5.3. Fertile or not-fertile: the million dollar question

On a tectonic perspective, typical Cu–Au porphyry deposits form preferentially (but not only) in destructive plate margins where they genetically relate with hydrous (up to 6 wt. % H₂O), oxidized (Δ FMQ + 0 to + 2), intermediate to acid, shallow, arcrelated intrusions that upon decompression exsolves fluids and volatile phases responsible for mobilizing siderophile and chalcophile elements under chlorine- or sulfate-bearing complexes and, ultimately, for their precipitation as ore metals (Richards, 2015a, 2011a; Sillitoe, 2010; Sobolev and Chaussidon, 1996; Sun et al., 2015). Interestingly, not all arc rocks are adequate for the formation of porphyry deposits and, in this regard, hypotheses involving the depth of intrusion, size of the pluton, redox state and water, sulfur and metallic contents of the magmas have been raised as potential players that might influence whether or not a given magmatic system is fertile (a good summary might be found in Zhang and Audétat, 2017). Sulfur speciation, as a consequence of magmatic fO_2 , stands as one of the most critical variable that dictates the characteristics of the porphyry mineralization (Sun et al., 2015). According to Richards (2015a), mantle melting in subduction zones under $fO_2 \ge$ Δ FMQ + 1 destabilizes residual sulfides and transfer their metallic content into the evolving melt. The optimal oxidation state, around Δ FMQ + 0 to + 2, may only be achieved through several million years of steady subduction. In essence, timing and tectonic context are crucial points to fully assess the metallogenetic potential of the igneous suites in the TMP.

The different igneous suites that encompass the OMS are interpreted as subduction related (e.g. Cassini et al., 2020; Juliani et al., 2002; Lamarão et al., 2005, 2002), and group i granitoids of ca. 2011 Ma represent the first batches of the arc-magmatism. These rocks are characterized by fO_2 values close to or below Δ FMQ, which are lower than the typical range for arc rocks (Δ FMQ + 0 to + 2). By combining its redox state with the pyroxene-bearing petrologic evolution, group i granites and granodiorites represent an unfertile stage of the arc-magmatism for the formation of typical Cu – Au magmatic-hydrothermal mineral deposits. In fact, group i rocks show negligible hydrothermal alteration (minor and localized K-metasomatism) and lack any trace of mineralization (Cassini, 2016).

Group ii granitoids, identified in the Tocantinzinho, Chapéu do Sol, Coringa, São Jorge and Patrocínio deposits, show higher fO_2 (Δ FMQ + 0 to + 4) and a petrologic trend compatible with amphibole fractionation, characteristics that indicate the evolution of the arc-magmatism towards more hydrous, oxidized and metallogenetic fertile conditions. The granodioritic porphyry (USP14-144) dated at 1986 Ma is also accompanied by younger granitoids, evidencing a protracted magmatic history behind group ii rocks (i.e. 1958 Ma for amphibole-bearing monzogranite from the Patrocínio deposit by Cassini (2016); 1979 Ma for the Tocantinzinho deposit syenogranites by Borgo et al. (2017); 1975 Ma for the Coringa deposit rhyolites by Tokashiki (2015)), a typical feature of porphyry forming plutons (Chelle-Michou et al., 2017; Large et al., 2018; Pirajno, 2009; Richards, 2015a). Group ii-hosted mineralizations are defined by disseminated gold bearing sulfides or by pyrite-quartz ±gold ±chalcopyrite veins and veinlets most often found in the sericitic and, less frequently, in the potassic and propylitic alteration zones. Early and late-stage hydrothermal alterations (sodic and argilic respectively), when present, are barren.

The high-K magmatism of group iii covers an age interval of approximately 20 Ma (1993 – 1974 Ma) and represents decompression melting of metasomatized mantle. Group iii rocks are rarer in the TMP, yet syenites and monzonites have been reported in the Patrocínio, Tocantinzinho, Coringa and São Jorge gold deposits. Our fO_2 estimates around Δ FMQ + 0 to + 2, combined with the pyroxene-bearing petrologic trend, assigns this group a low favorability for the formation of Cu – Au magmatic-hydrothermal systems. Interestingly, group iii rocks often show sericitic, potassic and carbonate hydrothermal alteration with disseminated, gold bearing, pyrite and pyrrhotite, features that we interpret as diagnostic of an interaction between the reduced, anhydrous and unfertile high-K magmas with the synchronous, hydrous, oxidized and metallogenetic fertile group ii melts.

There is a lack of data when it comes to mineralization age in the TMP and, in spite of the theoretical fertility of group ii granites (and group iii on a minor extent), Ar-Ar dating of alunite crystals points to mineralization age of 1.86 - 1.84 Ga, which is compatible with the YMS (ages from the V3 and Batalha deposits by Echeverri Misas (2015) and Juliani et al. (2005)). Whereas OMS represents the magmatic-arc sequence with oxidized and hydrous melts, YMS is compatible with the evolution of the system towards late-orogenic and collisional tectonic settings, a consequence of the progressive flattening of the subducting-slab, resulting in progressively anhydrous and reduced magmas (Fernandes et al., 2011; Fernandes and Juliani, 2019). During active subduction, the continuous sulfur influx through the mantle enables a high f_{S_2} , which stabilizes gold- and copper-rich residual sulfides. When subduction stalls, subsequent mantle melting (likely involving metasomatized SCLM), triggered due to astenospheric upwelling or orogenically thickened crust, will efficiently destabilize the previously formed sulfides and mobilize their metallic content into the generating melt (Richards, 2015a, 2011a). Hence the association of gold-rich porphyry deposits with late-orogenic

or collisional magmatism such as the YMS (Chen et al., 2015; Hou et al., 2013; Richards, 2015b). The Batalha and Palito deposit (and possibly the younger São Jorge granite) are hosted by the Parauari Intrusive Suite that coupled with the volcanics of the V3 deposit (Iriri Group) represent the first batches of the YMS (ca. 1.89 Ga). The first two deposits show the greatest concentration of disseminated gold and gold bearing sulfide veinlets in the sericitic alteration zone and, secondarily, on the propylitic and argilic zones. The associated granitoids show features (metaluminous to mildly peraluminous, high-K to shoshonitic, more evolved Nd isotopes than OMS and > 2.0 Ga inherited zircon grains) that suggest a mutual role of metasomatized mafic and crustal sources (Cassini et al., 2020; Echeverri Misas, 2015; Santos et al., 2004). The V3 deposit is hosted by rhyolites compatible with a stronger crustal contribution in primary SCLM magmas (ferroan, peraluminous, alkali-calcic to calc-alkalic). Mineralization is found in hydrothermal breccias in a shallower stratigraphic level of the system, and consists on alunite- and gold bearing sulfide veinlets distributed on the advanced argilic alteration, with lower sulfide concentrations on the potassic, propylitic and sericitic alterations.

In summary, despite their predominantly anhydrous characteristic, the first pulses of YMS are intimately related with gold-rich (gold-only?) magmatichydrothermal mineral deposits as a result of remobilization of SCLM and/or lower crust residual sulfides. Hence, the Parauari Intrusive Suite and the initial pulses of the Iriri volcanism may be considered as potentially fertile for the generation of gold-rich magmatic-hydrothermal mineral systems.

3.5.3.1. What the Sr/Y ratio tell us?

Over the past decade much attention has been driven to the relation between high Sr/Y rocks and porphyry Cu – Au deposits (i.e. most calc-alkaline, arc- and porphyry related magmas found in Andean-type subduction zones show high Sr/Y ratio), even though the origin of such relation remains in dispute. Some authors (e.g. Mungall, 2002; Sun et al., 2015) defend that high Sr/Y arc-rocks are genetically related with slab-melting and should be understood as high-silica adakites (Moyen 2009).

However, thermal modelling of subduction zones (e.g. Bouilhol et al., 2015) reveals that slab melting is rare and unlikely to be a major contributor for arc-magmatism, neither is garnet an abundant restitic phase upon mantle melting. An alternative explanation suggests that the adakitic signature of arc-magmas relates with the magmatic evolution itself and relies primarily on the timing of amphibole and plagioclase fractionation (Chiaradia et al., 2012; Loucks, 2014; Richards, 2011b). High Sr/Y rocks experienced early amphibole extraction and is typical of magmas with ≥ 4 wt. % H₂O that evolved at mid-crustal depths. On the other hand, if plagioclase precedes amphibole extraction, the case for less hydrous and shallower developed magmas, the system will be Sr depleted and the result will be low Sr/Y magmas.

More recently, special attention has been driven to alkaline, high-K to shoshonitic, low Sr/Y magmas, intruded in late- to post-subduction environments, the geologic scenario that frames TMP's context. World-known deposits such as Cadia Au -Cu porphyry (eastern Australia), the Bingham Canyon Cu – Mo – Au porphyry (eastern USA) and the Ok-Tedi Au – Cu porphyry (Papua New Guinea) are found in such geologic and tectonic contexts (Cloos et al., 2005; Cooke et al., 2013; Grondahl and Zajacz, 2017; Holliday et al., 2002; Richards, 2009). Chiaradia (2012) explains the Sr/Y ratio of a given magma with basis on the depth of evolution. Accordingly, intermediate composition magmas evolving at depths greater than 0.2 GPa will stabilize amphibole prior to plagioclase and magnetite, which yields high Sr/Y. Such magmas might eventually ascend through the crust and reach shallower depths, ultimately exsolving fluids and volatiles necessary to form magmatic-hydrothermal mineral systems. On the other hand, if the same magma undergoes a rapid decompression, plagioclase and magnetite will precede amphibole crystallization, yielding low Sr/Y and less hydrous magmas. In addition, magnetite-induced sulfide saturation will deplete the system in chalcophile elements prior to fluid exsolution, resulting in economically barren magmas. Chiaradia's model adequately explains the low Sr/Y of OMS's group ii granitoids, that still show reasonable fO_2 for the formation of porphyry Au – Cu deposits and is compatible with amphibole, more likely on a late stage of the crystallizing sequence. The YMS marks a transition from evolved-arc to post-orogenic or collisional tectonic settings and, with the exception of intermediate V3 volcanics,

amphibole is absent in all units, implying in anhydrous magmas with low Sr/Y. However, as mentioned on the previous section, YMS's petrogenesis involves remobilization of subduction-modified mantle and possibly lower crust, which confers this magmatic sequence its metallogenetic potential for gold-rich magmatichydrothermal mineral deposits.

3.6. Conclusions

The relevance of this study regards how the tectonic context translates into metallogenetic potential for base and precious metal occurrences in south-central Amazonian Craton. Results acquired allowed a better understanding on the magmatic evolution and on the tectonic context of the host rocks from selected mineral deposits in the Tapajós Mineral Province (TMP). Discussion and conclusions might be understood as a first step towards a unified metallogenetic model for the magmatic-hydrothermal mineralizations in the TMP. The different mineralizing systems are hosted either by igneous suites of 2.00 - 1.95 Ga, designated as the older magmatic sequence (OMS), or by igneous suites of 1.90 - 1.86 Ga, treated as the younger magmatic sequence (YMS).

OMS rocks might be divided into three groups. Group i correlate with the Cuiú-Cuiú Complex and comprises peraluminous granites and granodiorites that represent the first batches of arc-magmatism on the TMP (granodiorite sample dated at 2011 Ma), which is characterized by a strong crustal component and an oxidizing and dry petrologic evolution. The $X_{Ce^{4+}}^{melt}/X_{Ce^{3+}}^{melt}$ zircon-based oxy-barometer indicate fO_2 values close to the FMQ buffer (– 4 ≤ Δ FMQ ≤ + 0). However, due to its anhydrous trend these rocks show a low favorability for the formation of magmatic-hydrothermal mineral systems.

Group ii rocks are common and widespread in the TMP, correspond to the Creporizão Intrusive Suite, comprises metaluminous to peraluminous granites (s.l) that evolved on an amphibole and magnetite bearing trend, and represents the evolution of the arc-magmatism. The granodioritic porphyry dated at 1986 Ma represents this stage, which is characterized by the lowest magmatic temperature 768 °C. fO_2 constraints corroborate the more oxidized trend for these rocks ($0 \le \Delta FMQ \le + 4$), rendering their potential fertility for the formation of porphyry Cu – Au mineralizations. The low Sr/Y ratio reflects a rapid decompression, enabling plagioclase fractionation prior to amphibole extraction in spite of hydrous magmas. On the field, group ii rocks are commonly affected by hydrothermal alteration, with disseminated gold or gold and chalcopyrite bearing veins and veinlets most commonly found on the sericitic zone, with potassic and propylitic alterations also economically relevant and barren sodic and argilic alterations.

Group iii comprises lower silica, high-K, metaluminous, ferroan, reduced and anhydrous quartz-syenites and monzonites of 1993 and 1974 Ma, generated through decompression melting of metasomatized mantle, which yields high magmatic temperatures (TZirc.Ti from 786 to 811 °C). These rocks are rarer and have only been reported in the Patrocínio and Coringa deposits (southern TMP) on drill core sampling. fO_2 between $\Delta FMQ = 0$ and + 1 positions these rocks on an intermediate redox state within OMS. Its reducing petrologic trend indicates that, by itself, group iii should not be considered economically fertile. Nevertheless, the group's metallogenetic potential lies on its interaction with the coeval, more hydrous and oxidizing group ii melts. The end products are syenites and monzonites affected by sericitic, chloritic and carbonate alterations with disseminated pyrrhotite-pyrite ±gold with less frequent gold bearing pyrite veinlets.

YMS comprises rocks from the Parauari Intrusive Suite and from the Iriri Group, and is represented in the Batalha, Palito, São Jorge and V3 deposits. Field relationships between the older and younger sequences are rare, but Iriri volcanics are found as dykes within OMS granitoids or define lava-flows, whereas the intrusive units define round-shaped plutons. Whereas intermediate V3 volcanics share similar geochemical features with the OMS, acid V3 and the Batalha and Palito granitoids are essentially ferroan and evolved on a magnetite- and amphibole-free trend, suggesting anhydrous and reduced parental magmas. We interpret such differences as symptomatic of a changing tectonic framework within the TMP, from magmatic-arc (OMS) to a post-

orogenic or collisional setting. As subduction stalls (or upon the progressive flattening of the slab) magmatism gets dryer, comparatively reduced and, in theory, less favorable for the formation of magmatic-hydrothermal mineral deposits. However, YMS' metallogenetic potential is related with remobilization or melting of SCLM and/or lower crustal, gold-rich sulfides formed on the previous magmatic events. The outcome is identified in the Batalha and Palito deposits, with disseminated gold and gold bearing sulfide veinlets preferentially distributed in the sericitic zone, and in the V3 mineralization, with alunite and gold bearing sulfide veinlets hosted by hydrothermal breccias on the advanced argilic alteration. Therefore, YMS should be treated as metallogenetic fertile for the formation of gold-rich magmatic-hydrothermal systems, since it efficiently mobilizes previously formed sulfides.

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4. Discussion

4.1. Topics and Considerations on Classification Diagrams

A few problems arise when dealing with classification of igneous rocks in the TMP. Both thick weathering profile and widespread hydrothermal alteration might hinder a reliable petrographic- or whole-rock geochemistry-based classification (Fig. 13 exemplifies the empirical effects of both processes). Samples J-35 and J-36 are intermediate and undifferentiated intrusive rocks described by Tokashiki (2015) at southern TMP that show a considerable degree of weathering likely due to leaching of soluble major oxides as Na₂O, K₂O and CaO (Fig. 13a). As a result, plotting these samples on Total Alkali vs. Silica (TAS) diagrams (Cox et al., 1979; Middlemost, 1994) might render unrealistic or unreliable classifications (Figs. 13b and 13c). This effect tends to be soothed on the R1-R2 plot by De la Roche et al. (1980), which comprises all major rock-forming elements in millications (highly mobile Na and K are balanced against other major elements). As a result, De la Roche's classification diagram should be preferentially used since it yields a more reliable discrimination of intrusive and extrusive rocks. The weathering effects on granites are also represented on the plots from Figure 13 (samples Fbt-3/7b and CJ-33 from the Batalha and Palito deposits plot close to the W vertice, out of range on Cox's and De la Roche's plots and close to the granodiorite-granite boundary on Middlemost's TAS.

Ideally, and despite its caveats (Bonin et al., 2020), the modal QAP classification (Streckeisen, 1976) should be applied in order to unbias the effects of hydrothermal alteration (i.e. secondary minerals originated due to K or Na-Ca metasomatism should not be considered on modal classification). Samples DT-07b and Fbt-2/7b demonstrate the effects of hydrothermal alteration on granitic rocks on the TMP. Both lack the weathering geochemistry signature (Fig. 13a) and are described as granites affected by Na- and/or K-metasomatism (Echeverri Misas, 2010; Juliani et al., 2002) which translates into granodiorite and granite on the TAS diagram after Cox et al. (1979) (Fig. 13a), or quartz-monzonites on the TAS diagram after Middlemost (1994) (Fig. 13b), or tonalite and syenite on R1-R2 plot after De la Roche et al. (1980) (Fig. 13c).





Fig. 13. MWF plot (13a) (Ohta and Arai, 2007) and classification diagrams after Cox et al. (1979) (13b); Middlemost (1994) (13c); and De la Roche et al. (1980) (13d) for weathered and hydrothermally altered rocks.

Cassini (2016) also demonstrated how monzo- and syenogranites described on petrography might be geochemically classified as K-richer granitoids, yielding fake- or episyenites (Suikkanen and Rämö, 2019). However, the QAP classification may not be the best option when dealing with a robust database, which could render the task practically unrealistic. As demonstrated by Bonin et al. (2020) modal and chemical composition of igneous rocks are not easily overlapped and, for this reason, De la Roche's R1-R2 diagram is used in this study with a mere descriptive objective. Petrogenetic constraints were based on aluminosity and radiogenic isotopes as will be demonstrated on the following sub-sections.

Part III - Discussion and Conclusions

As for aluminosity, preference was gave to the A-B plot after Debon and Le Fort (1983), revisited by Villaseca et al. (1998). The classic A/CNK vs. A/NK plot (mol% oxides) introduced by Shand (1943) adequately mirrors the excess or deficit of the system in Al after feldspar extraction. However, since it is the intention of this contribution to access the petrologic evolution of the rocks and how they relate to each other, it is convenient to plot aluminosity against a differentiation index, adequately mirrored by maficity on the B axis. On the B-A plot, the A > 0 domain is divided with basis on the intensity of peraluminosity, which brings relevant petrogenetic implications as will be demonstrated.

Moreover, the widely used Pearce diagrams for discriminating tectonic setting based on trace-element content (Y, Nb, Rb, Yb and Ta) of granitic rocks might render important discussion but it lack robustness by itself since these element abundances are intimately related with the accessory mineral content (zircon, apatite, monazite, allanite etc). Granitic rocks or magmas might undergo innumerous modification processes after mantle and/or crustal melting (i.e. differentiation, assimilation, hybridization etc) ultimately resulting in newer and evolved compositions that no longer mirrors their parental magmas nor the original tectonic context (Annen et al., 2015, 2006; Bonin et al., 2020; Moyen et al., 2017). Hence, tectonic-setting diagrams should be used with caution and, ideally, supported by additional data.

4.2. Genesis of TMP Magmas (the older and younger magmatic sequences)

The results acquired in this study, coupled with whole-rock geochemistry data available in the bibliography, allowed the separation of the Orosirian units in the Tapajós Mineral Province (TMP) into the older- (OMS) and younger magmatic sequences (YMS), respectively 2.0 – 1.95 Ga and <1.89 Ga. The older magmatic sequence is divided in group I, II and III granitoids, with rhyolites associated, whereas YMS is represented by the Iriri volcanics, Parauari (PAR) and Maloquinha Intrusive Suites (MLQ).

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The first bursts of magmatism in the Tapajós Mineral Province (TMP) refer to the ca. 2.0 Ga granitoids of the Cuiú-Cuiú Complex that belong to group I granitoids, represented by the 2011 Ma granodiorite (sample USP14-160). This sample shows evolved $\epsilon Nd_{(t)} = -8.36$ (similar results were also reported by Echeverri Misas, 2015 and Sato, 1998), high TZirc.Sat (798 °C), belongs to a series characterized by preferentially peraluminous samples and by a great proportion of inherited zircon cores, indicating a strong crustal component for the formation of these magmas. These data appear to support the tectonic model proposed for the Amazonian Craton by Carneiro et al. (2019) and by Juliani et al. (2015), that defend the existence of Archean basement on the Tapajós region. Yet, direct evidence of > 2.5 Ga crust on the TMP region is restricted to one zircon grain (Santos et al., 2004). Geochemical modelling for group I shows an evolution compatible with plagioclase (68%), biotite (16%), magnetite (7%), titanite (3%) and clinopyroxene (6%) fractionation, which defines an anhydrous petrologic evolution towards high Sr/Y and La/Yb. Zircon petrochronology enlightens in more detail the evolution of these rocks. Hf-enriched zircon cores reflect episodic injections of new magma batches within the magmatic chamber, and partially corroded, rounded edges and the low whole-rock Zr content of this sample (179.6 ppm) suggest early extraction of the mineral. Titanite fractionation render the positive to subtly negative Eu anomalies and the low Th/U ratio observed on the zircon grains (Fig. 11) (Harrison et al., 2007b; Lee et al., 2020; Loader et al., 2017). The fO₂ estimates point to values close to or a few log units below the FMQ buffer ($-4 \le \Delta FMQ \le +0$), just enough to stabilize magnetite (Fig. 12b). These geochemical attributes mark the onset of the subduction process on the TMP region at ca. 2.0 Ga, where oxidizing components were introduced on mantle wedge melts that got subsequently contaminated by overlaying crust on deep-seating hot-zones and/or by subcrustalerosion material (Fernandes and Juliani, 2019; Juliani et al., 2015).

The secondary pulses of the arc magmatism (or group II granites, dated at 1986 Ma) are markedly different and cover a vaster area on the TMP. After its first phase, arc-magmatism got less contaminated by continental crust, fact that translates into moderately negative $\epsilon Nd_{(t)}$ acquired for CRP granites and synchronous volcanics of ca. 1.97 Ga (averages of -2.77 and -1.87 respectively). Aluminosity also individualizes the

first phase (or group I granites) from its evolution, suggesting the role of different melting sources (Clemens et al., 2011; Clemens and Stevens, 2012; Villaseca et al., 1998). Whereas group I comprises peraluminous samples, group II rocks define a negative slope on the A-B diagram (Fig. 5c), with samples that vary from metaluminous to mildly peraluminous on the more evolved members. The trend is typical of subduction-related granitoids and is compatible with the presence of mafic parental magmas, understood as a mantelic heritage. Geochemical modelling shows an evolution compatible with a granodioritic liquid that evolved to alkali-granite composition. Such petrologic evolution is consistent with fractionation of plagioclase as the most abundant phase (up to 55% of the cumulate composition), which is accompanied by K-feldspar (10%), amphibole (30%), titanite (3%) and magnetite (2%), for a F_c of 0.43 to 0.57, a monzonitic cumulate and $R^2 = 0.083$ (Cassini et al., 2020). Geochemical and timing equivalencies, allowed the interpretation of the volcanic sequence described by Tokashiki (2015) in southern TMP as the extrusive manifestation of the CRP magmatism. As demonstrated by Chiaradia et al. (2012), Grove et al. (2012) and Loucks (2014), in H_2O -rich arc-related magmas (≥ 4 wt. % H_2O), amphibole precedes plagioclase extraction, resulting on high Sr/Y (and La/Yb) rocks (Fig. 9). On the other hand, if plagioclase precedes amphibole extraction, the case for less hydrous and shallower developed magmas, the system will be Sr depleted and the result will be low Sr/Y magmas. According to Annen et al. (2015), the main differentiation mechanism that controls granitic magma generation is fractionation of the primary mafic magma. This process is usually erratic and occurs in many stages, where a batch of more primitive andesitic magma is injected into a more differentiated dacitic crystal mush at shallower hot zones. This concept and model accounts for many of the field relations described in the TMP such as mutually intrusive bodies, diffusive or unclear contact, ubiquitous mafic enclaves and rarer rapakivi textures.

Zircon petrochronology also allows important petrologic constraints on group II rocks. Sample USP14-144 (granodioritic porphyry) is characterized by elongated zircon grains and a synchronicity between core and rims U-Pb dating, suggesting rapid zircon crystallization which is compatible with a shallow crustal level intrusion (<4 km depth). Plagioclase fractionation explains the evolution towards lower zircon Eu/Eu* as Zr/Hf

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decreases and, the few samples with higher Eu/Eu* reflects competing titanite extraction. Amphibole and titanite fractionation explains the steeper array on the Th/U vs. Dy/Yb plot (Fig. 11) and low magmatic temperature (TZirc.Ti = 768 °C). Furthermore, the oxidized condition of group II magmas is supported by geochemical modelling and fO_2 values between Δ FMQ +0 and Δ FMQ +4 (Fig. 12).

The high-K and low silica facies of CRP (syenites and monzonites dated at 1993 and 1974 Ma) defines group III granitoids. They are comparatively rarer in the TMP, but have been reported in the Patrocínio, Tocantinzinho, Coringa and São Jorge deposits. The rocks are metaluminous to peraluminous, ferroan, alkalic (Fig. 5), are characterized by $\epsilon Nd_{(t)}$ from -1.64 to +1.69 and are understood as differentiated batches of juvenile material with negligible crustal contribution. Geochemical modelling reveals a petrologic evolution compatible with crystallization of K-feldspar as the major phase (up to 64% of mineral proportion on the cumulate), followed by plagioclase (20%), biotite (7%), apatite (4%), clinopyroxene (3%) and ilmenite (2%), for a F_c within the range 0.33 – 0.37, and a K-feldspar rich cumulate. Such evolution is dryer when compared with group II granites, where the cumulate has approximately 30% of amphibole. This suggests that group III rocks evolved through early extraction of plagioclase which is symptomatic of anhydrous melts and explains the Eu anomalies (negative), Sr and Ba depletions, and low Sr/Y and La/Yb ratios. Another important difference between groups II and III granitoids regard their iron-oxide mineral phase. Geochemical modelling shows that magnetite is incompatible on the petrologic evolution of group III and is only suitable on the evolution modeled for the group II granites. Despite their equivalent alumina saturation index (metaluminous to mildly peraluminous), syenites are characterized by positive $\varepsilon_{Nd(t)}$ which represents early differentiated batches of magma provided by the corner flow induced, metassomatized mantle wedge melting with practically no crustal contamination. On the bibliography, these rocks are treated as K-rich calc-alkaline granitoids (Bonin, 2004, 1990; Bonin et al., 2020) or as Fe-K granitoids (Laurent et al., 2014). Despite their abundance in Proterozoic terrains throughout the world (Ferré et al., 1998; Ferreira et al., 1998; Bogaerts et al., 2006; Kouankap Nono et al., 2010; Vander Auwera et al.,

2011; Laurent et al., 2014), the precise petrogenetic mechanism behind group III granitoids remains unclear debatable.

Zircon geochemistry for samples USP14-83, 136 and 91 enlightened the petrologic trend for group III's syenites and monzonites. USP14-91 (syenite) marks the onset of the high-K magmatism at ca. 1993 Ma (Fig. 10). This sample presents low silica content (60 wt.%) and zircon saturation is due to the high whole-rock Zr (357.7 ppm). In fact, Figure 12a indicates the predominance of autocrystic grains. Sample USP14-136 (monzonite) shares similar characteristics, yet, much younger magmatic age (1974 Ma) representing a late stage pulse of the high-K magmatism. Inherited zircon grains dated at 2055 Ma reflect a protracted residence period on deep hot zones by the primary magmas, which explains the positive to slightly negative $\epsilon Nd_{(T)}$ acquired for group iii rocks (Tab. 3 on Lithos paper available as supplementary material). Sample USP14-83 represents aplitic dykes that mark the evolution of the high-K magmatism. Its low whole-rock Zr content (127.4 ppm) suggests previous zircon extraction and, consequently, the 1987 Ma age (Fig. 10e) should be understood as inherited (Fig. 12a suggests the predominance of antecrystic zircon grains). Unrealistic fO_2 constraints of Δ FMQ +2 or greater (Fig. 12b) for this sample are the product of inherited zircon grains, hydrothermal alteration and/or mineral inclusions on the ablated spot (anomalous LREE enrichment is evidenced on the LREE index vs. Ti plot from Fig. 11c) (Bell et al., 2019, 2016). Low Eu/Eu* negates titanite fractionation and the subtle drop on Dy/Yb as Th/U decreases supports a dry, amphibole-absent, ilmenite- and pyroxene-bearing evolution modeled for group iii. Its reducing affinity, as pinpointed by geochemical modeling, is also supported by the fO_2 estimates of Δ FMQ +0 to +1. Additionally, the higher magmatic temperatures acquired for group iii syenites and monzonites (786° to 811° C) attest the dry characteristic of the high-K magmatism.

These findings also enlighten the debate on the tectonic mechanisms that operated during the Paleoproterozoic. As pointed out, OMS rocks are different the typical Archean and TTG dominated continental crust. Group I and II granitoids show geochemical evidence of arc-related rocks (vary from metaluminous to peraluminous, calc-alkalic, magnesian to ferroan and show evolved Nd isotopes). Group I evolved through pyroxene and magnetite extraction at ca. 2.0 Ga, and evolves to more hydrous

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and oxidized magmas (group II) as the arc matures at ca. 1.98 Ga. These characteristics indicate that on the Rhyacian-Orosirian transition, oxidizing agents were being progressively recycled and transferred into the generated magmas, making magnetite a more abundant phase (with magmatic fO_2 up to Δ FMQ +4), which strongly suggests similar tectonic and petrogenetic mechanisms as seen in modern Phanerozoic magmatic arcs. Similar results and tectonic implications have been recently published by Meng et al. (2021) for the ca. 1.88 Ga, Haib porphyry Cu deposit in southern Namibia. Interestingly, the results presented in this thesis are slightly older and allow the connection between OMS and the ultimate cycles of atmospheric oxygen buildup known as the great-oxidation-event (e.g. Gumsley et al., 2017) that affected the planet from early- to mid-Paleoproterozoic. These findings coupled with the results and ideas from Evans and Tomkins (2011), Meng et al. (2021) and Richards and Mumin (2013) provide relevant and robust data that tectonic and metallogenetic processes as seen on Phanerozoic terrains also operated on the Paleoproterozoic.

The first batches of YMS magmatism is represented by the ca. 1.90 granites of the Parauari Intrusive Suite (PAR), approximately 70 million years younger than CRP. PAR guards similarities with OMS rocks (e.g. metaluminous to mildly peraluminous rocks), yet, most prominent differences regard PAR's alkali-calcic, essentially ferroan and much narrower compositional range (Fig. 4). Geochemical modelling shows an evolution compatible with albitic-plagioclase (44%), K-feldspar (42%), pyroxene (7%), titanite (3%) and apatite (4%) extraction, generating an alkali-granitic liquid and a syenite cumulate, characterizing an anhydrous and reducing evolution. This trend drives the evolving magma towards lower Sr/Y, La/Yb and Eu/Eu* ratios (Fig. 9). Moreover, the suite shows more strongly negative $\epsilon Nd_{(t)}$ (average of -4.85) when compared with OMS' group II and III granitoids, which could be the result of crustcontaminated or metasomatized mantle melting. PAR's precise tectonic setting, however, is hard to interpret based on its geochemistry signature. Its high-K to shoshonitic, ferroan, alkalic-calcic affinity and the presence of metaluminous samples on the least evolved spectra is compatible with reduced mafic parental magmas on a late-, post-orogenic or collisional tectonic setting, where igneous petrogenesis involves previously metasomatized mantle melting. According to Bonin (1990), a typical

orogenic rock association will comprise igneous suites directly involved with hydrated mantle-wedge melting that transitions to alkaline magmatism through collision-related high-K magmatism on an age span usually shorter than 100 Ma. Within this context the alkaline suites (divided into post-orogenic and early-anorogenic alkaline granites) commonly overlap in age the last pulses of the arc-related sequence. Regardless of its precise tectonic scenario, PAR's geochemical attests a transition from hydrous and oxidizing (amphibole and magnetite bearing granites) to anhydrous and reducing magmas.

The volcanic rocks of the Iriri Group (1.89 – 1.87 Ga) show geochemistry characteristics that partially resemble the PAR granitoids. In fact these rocks overlap in age and represent the onset of the YMS. The rocks vary from metaluminous to peraluminous, alkalic to calc-alkalic and are magnesian on the lower silica side and ferroan on the more acid members, geochemical attributes that suggest oxidized to reduced mafic parental magmas with contribution of preexisting crust. Mildly negative εNd_(T), however, indicate a greater contribution from juvenile sources (Cassini et al., 2020). Geochemical modelling shows a discontinuous petrologic trend within the Iriri Group. Accordingly, intermediate facies of Iriri evolved through K-feldspar, amphibole, anorthite-rich plagioclase and biotite extraction, which drives the evolving magma towards higher Dy/Yb, Sr/Y and La/Yb ratios. The acid spectra of Iriri, on the other hand, defines a trend compatible with a rhyolitic initial composition that differentiates to alkali-rhyolite through fractionation of albitic-plagioclase, K-feldspar, pyroxene and titanite, with a syenite cumulate (an evolution similar to the one modeled for PAR granites, Fig. 7). Besides the magnetite-free evolution, acid Iriri and PAR evolved on an amphibole-absent trend, which reinforces a change on the tectonic framework of the TMP. The predominantly hydrous and oxidized melts from OMS were possible due to an active subduction-zone that provided slab-derived fluids and oxidizing agents to the mantle wedge. The geochemistry features of PAR and Iriri contrasts with OMS and suggests that subduction-modified mantle is the most likely source for the ca. 1.88 Ga magmatism on the TMP region.

The Maloquinha Intrusive Suite (MLQ, ca. 1.87 Ga) represents the final pulses of YMS. It is compositionally homogeneous and varies from metaluminous to highly

peraluminous alkali-granites that indicate a greater proportion of incorporated lower crust components and peritectic minerals (possibly garnet?) by primary magmas. Geochemical modelling shows an evolution that starts from a granitic initial composition that evolves to alkali-granite through extraction of plagioclase (36%), Kfeldspar (36%), clinopyroxene (25%) and ilmenite (3%). According to the geotectonic model proposed by Fernandes et al. (2011), around 1.88 Ga the TMP was affected by flat-subduction event that metasomatized the lithospheric mantle. Magma generation in this context would involve the directly underthrusted subcontinental-lithosphericmantle (SCLM), severely metasomatized by the previous events. This tectonic setting would generate high-K and metaluminous primary magmas that shift to higher aluminosity upon crustal contamination. The ultimate result translates into the close to zero or slightly negative $\epsilon Nd_{(T)}$ (between -2.64 and -0.28) acquired for MLQ. As proposed by Bonin (2004), high-K igneous suites are genetically related with phlogopite-bearing and metasomatized lithospheric mantle melting, that will commonly present crustal contamination as it ascends. MLQ shows similar geochemical and petrologic characteristics with the Fe-K igneous suites of the Matok pluton located at northern Kapvaal Craton (Laurent et al., 2014). The authors understand the pluton's composition as an intermediate member between Mg-K sanukitoids and A-types granites that would be the result of differentiation of a parental mafic magma whose petrogenesis would involve melting of both metasomatized SCLM and asthenosphere. With the suppression of the subduction process, on a continent-continent collisional setting, either slab-breakoff, slab-retreat or SCLM delamination could result in asthenospheric mantle inflow and, in this case, SCLM melting would be a consequence of the increasing thermal anomaly, a tectonic scenario that is an analogue for MLQ petrogenesis. Ascension of magma for the formation of both MLQ and late pulses of Iriri magmatism is particularly enhanced by the continental-crust extension due to astenospheric upwelling (Fig. 10d). In fact, it is exactly at this tectonic stage that the São Gabriel AMCG association (central Amazonian Craton) is formed (Valério et al., 2018). Even though the precise petrogenetic processes that involve MLQ still require further investigation, the tectonic implication of its geochemistry signature is invariable. It marks the shift of the tectonic

setting from a post-collisional or post-orogenic to an early-anorogenic tectonic setting, with increasing degrees of crustal signature on originally metaluminous SCLM melts.

4.3. Metallogenetic Potential of the Igneous Suites

Both whole-rock and zircon geochemistry allowed constraining the most and least fertile suites for the formation of Cu – Au magmatic-hydrothermal mineral systems. The first pulses of OMS magmatism at ca. 2.0 Ga are included on group I granitoids. These are characterized by a strong crustal component and a magnetiteand pyroxene-bearing petrologic trend that coupled with fO_2 estimates close to or below Δ FMQ positions group I slightly below the optimal oxidizing window for typical porphyry Cu – Au deposits (Δ FMQ +0 to +2, Sun et al., 2015). This indicates that despite the presence of small amounts of magnetite, the subduction process still needed to reach its maturity in order to generate more hydrous and higher fO_2 magmas. As a consequence, these rocks lack the geochemistry attributes of typical ore-forming plutons and should be understood as metallogenetic unfavorable.

As stated by Richards (2015a) it may take tens of million years after the onset of subduction so arc-related magmas can acquire their characteristic oxidized signature ($\geq \Delta$ FMQ +0.5). OMS's group II granitoids represent the evolution of the magmatic-arc (granodioritic porphyry dated at 1986 Ma), that according to the modeling results evolved through amphibole and magnetite fractionation. The fO_2 estimates of Δ FMQ +0 to +4 lends support to the oxidized conditions of group II magmas, that consequently should be understood as metallogenetic fertile. Not surprisingly, the Patrocínio (Cassini, 2016), Tocantinzinho (Borgo et al., 2017) and the Coringa deposits (Tokashiki, 2015) are hosted by OMS rocks, where mineralization is defined by disseminated gold bearing sulfides or by pyrite-quartz ±gold ±chalcopyrite veins and veinlets most often found in the sericitic and, less frequently, in the potassic and propylitic alteration zones.

The high-K and low silica rocks of group III (quartz-syenites and monzonite of 1993 – 1974 Ma) represent metasomatized mantle melts that evolved on a pyroxene-

and ilmenite-bearing trend. Zircon-based fO_2 estimates around Δ FMQ +0 to +2 position these rocks on the reduced spectra of the magmatic-arc which, in theory, represent unfertile plutons. On the field, however, group III rocks often display hydrothermal alteration (sericitic, potassic and/or carbonatic) with disseminated, gold bearing, pyrite and pyrrhotite, despite its reduced characteristic. Such features suggests that group III magmas interacted with the more oxidized, hydrous and metallogenetic fertile group II melts, ultimately generating the textural relations, hydrothermal alteration and mineralized syenites and monzonites.

Despite the theoretical potential of group II and III granitoids for the formation of magmatic-hydrothermal mineral deposits, the available data point to mineralization age of 1.86 – 1.84 Ga (Ar-Ar dating of alunite crystals by Echeverri Misas (2015) and Juliani et al. (2005), that macthes YMS timing.

Whereas OMS represents the magmatic-arc sequence, with oxidized and hydrous melts, YMS represents the evolution of the tectonic framework towards lateorogenic and collisional tectonic settings. During active subduction, the continuous sulfur influx through the mantle enables a high fS_2 , which stabilizes gold- and copperrich residual sulfides. When subduction stalls, subsequent mantle melting will destabilize previously formed sulfides and mobilize their metallic content into the generating melt (Richards, 2011a, 2015a). For this reason, late-orogenic or collisional magmatism such as part of the YMS, are prone for the formation of gold-rich porphyry deposits (Hou et al., 2013; Chen et al., 2015; Richards, 2015b). In fact, both the Batalha and Palito deposits (and possibly the younger São Jorge granite) are hosted by the PAR granites that represent the first batches of YMS (ca. 1.89 Ga). The hosting granites are metaluminous to mildly peraluminous, high-K to shoshonitic, show more evolved Nd isotopes than OMS and > 2.0 Ga inherited zircon grains, all suggesting a mutual role of metasomatized mantle and crustal sources on a post-orogenic or collisional tectonic setting (Santos et al., 2004; Echeverri Misas, 2015; Cassini et al., 2020). Iriri volcanics host the epithermal (high-sulfidation) V3 gold deposit. The rocks are ferroan, peraluminous, alkali-calcic to calc-alkalic compatible with a stronger crustal contribution in primary SCLM-derived magmas, also compatible with a post-orogenic or collisional tectonic setting.

5. Conclusions

The efforts applied in this study focused on unrevealing how the Orosirian suites evolved on the Tapajós Mineral Province (TMP), the given tectonic setting behind the suites and how these parameters translate into metallogenetic fertility. Two methods were applied: whole-rock geochemistry, which includes unpublished data and results available on the bibliography; and new in-situ trace-element measurements and U-Pb dating in zircon grains, which allowed further petrogenetic and geochronology constraints.

The results allowed the individualization of two main age groups in the TMP, the older-(OMS, 2.0 – 1.95 Ga) and younger magmatic sequences (YMS, 1.89 – 1.86 Ga). Within the OMS, three group of granitic rocks (with minor extrusive equivalents) are individualized:

- Group I marks the onset of subduction-related magmatism (granodiorite sample dated at 2011 Ma) and comprises peraluminous granites (s.s.) and granodiorites, characterized by highly evolved εNd_(T), and an anhydrous and slightly oxidized petrologic evolution (- 4 ≤ ΔFMQ ≤ + 0).
- Group II comprises metaluminous to peraluminous granites and rhyolites inserted on the 1.98 - 1.95 Ga interval (the granodioritic porphyry dated at 1986 Ma represents this stage of the arcmagmatism). These rocks evolved on an amphibole- and magnetitebearing trend ($0 \le \Delta FMQ \le + 4$) which indicates the presence of hydrous and oxidized mafic parental magmas and, consequently, the evolution and maturity of the arc-magmatism. Furthermore, group II granites are the units that cover the most area within OMS.
- Group III involves high-K, low-silica, ferroan and metaluminous quartzsyenites and monzonites (dated at 1993 – 1974 Ma) characterized by juvenile εNd_(T). Geochemical modelling reveals a reduced and anhydrous evolution compatible with pyroxene and ilmenite

fractionation. Despite its synchronicity with group II, group III rocks represent juvenile batches of magma as a consequence of decompression melting of metasomatized mantle.

Despite the heterogeneities and geochemistry variability involved in subduction related magmatism, the results acquired adequately explains (and predicts) the petrologic evolution and the composition of the evolving melts through fractional crystallization. Interestingly, the worst correlation for the fractional crystallization models (or highest R²) belongs to group I granitoids, that accordingly show the greatest evidence of crustal assimilation.

The YMS comprises rocks from the Iriri Group (1.89 – 1.87 Ga) and granitoids from the Parauari (PAR, ca. 1.89 Ga) and Maloquinha Intrusive Suites (MLQ, ca. 1.87 Ga).

- Iriri volcanic rocks are metaluminous to peraluminous, magnesian to ferroan and cover a vast compositional range (from andesites to alkalirhyolites). The intermediate facies evolved on an amphibole-bearing and magnetite-free trend. Acid volcanics, on the other hand, lacks amphibole and evolved a reduced trend, suggesting reduced and anhydrous parental magmas that significantly differ from OMS's source.
- PAR is synchronous with the first pulses of Iriri and comprises metaluminous to peraluminous, high-K to shoshonitic and ferroan granites that are characterized by evolved ɛNd_(T) (average of -4.85). These rocks evolved on a reduced and anhydrous trend that supports different sources for YMS magmas (most likely metasomatized mantle) as a result of a changing tectonic framework on the TMP, from subduction to a post-orogenic setting.
- MLQ defines the final pulses of YMS, represented by metaluminous to highly peraluminous alkali-granites that show slightly negative or close to 0 ɛNd_(T) and a reduced and anhydrous trend. These features are interpreted as the consequence of metasomatized SCLM melting after the flat-subduction event on ca. 1.88 Ga.

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By looking in detail to the acquired results, OMS's group II granites gathers the required features to be considered as metallogenetic fertile (i.e. metaluminous to peraluminous, magnesian to ferroan, hydrous and oxidized rocks), fact that is attested by the Patrocínio, Tocantinzinho and Coringa deposits. The YMS rocks evolved on a reduced and anhydrous petrologic trend that in theory would be economical metallogenetic unfertile plutons. Perhaps the most crucial point to be taken into account regarding the metallogenetic potential of the igneous suites in the TMP involves remobilization of previously formed gold-rich sulfides. As demonstrated, YMS petrogenesis invariably involves melting of subduction modified mantle sources and, consequently, the first pulses of the younger sequence (Parauari and Iriri volcanics) might be responsible for remobilization of residual sulfides and their metallic content, ultimately resulting in gold-rich magmatic-hydrothermal mineral deposits as exemplified by the Palito, Batalha, V3 and São Jorge gold deposits.

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Supplementary material I - Zircon Geochemistry

	Obs																												
Spot #	Core/	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Се	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
	Rim																												
83 - 1	Core	7.77	2.00	2030	530	486 800	7300	1.63	0.91	128. 0	69.0	28.0	18.0	33.0	21.0	5.9	4.2	198. 0	76.0	493	56	92	9	107 70	250	398	31	473	18
83 - 3	Core	12.0 4	0.67	713	17	440 000	1100 0	0.29	0.13	19.4	0.5	2.3	0.3	3.4	0.2	0.7	0.1	66.1	1.4	215	4	42	1	808 0	180	65	2	62	3
83 - 11	Core	7.75	0.64	1623	60	455 000	1200 0	24.8 0	6.20	310. 0	48.0	56.5	6.3	42.4	4.1	6.1	0.6	183. 0	11.0	373	10	68	2	961 0	220	342	16	257	7
83 - 16	Core	10.2 0	1.20	2271	52	485 000	1400 0	0.41	0.12	48.1	6.2	15.0	2.0	22.3	2.4	2.9	0.3	228. 0	6.9	536	22	95	3	921 0	290	345	15	193	14
83 - 21	Core	12.3 9	1.00	1471	49	501 000	1300 0	0.77	0.10	149. 0	16.0	13.5	1.6	17.2	1.5	2.4	0.2	128. 8	3.9	359	12	66	2	995 0	320	554	25	493	18
83 - 29	Core	11.0 3	0.99	2527	90	435 900	9500	1.00	0.16	214. 0	23.0	22.5	2.2	28.7	3.8	3.8	0.5	243. 2	8.8	552	15	100	2	828 0	180	534	24	367	13
83 - 37	Core	16. 88	1.4 0	1024	56	47 40 00	1500 0	0.8 4	0.0 5	17 0.8	6.7	14. 7	1.0	19. 1	0.9	3.3	0.3	11 5.5	3.9	24 4	7	44	1	93 50	25 0	23 0	8	17 5	5
83 - 50	Core	7.29	1.10	860	110	451 100	9300	0.80	0.28	112. 0	30.0	11.5	2.8	15.5	3.7	2.4	0.6	102. 0	14.0	224	14	41	3	981 0	210	184	12	173	5
83 - 62	Core	4.02	0.57	972	27	428 000	1100 0	1.18	0.77	91.0	7.4	7.6	1.7	9.4	1.2	1.2	0.2	88.3	3.8	277	7	54	2	958 0	320	309	8	401	10
83 - 7	Rim (i2)	6.39	0.86	746	36	411 400	9100	6.20	2.70	39.0	6.5	10.4	3.8	4.8	1.0	0.4	0.1	65.4	3.8	231	9	44	1	906 0	300	225	12	223	10
83 - 13	Rim	19.4 4	1.40	3490	220	490 800	7400	5.50	0.49	161 0.0	150. 0	78.5	5.7	107. 9	9.8	20.9	1.8	456. 0	47.0	589	54	97	7	112 10	340	844	48	322	12
83 - 17	Rim	10.3 2	0.87	1680	130	469 000	1600 0	3.69	0.53	274. 0	32.0	63.0	5.8	68.5	6.4	11.2	1.1	211. 0	17.0	329	17	56	3	988 0	270	681	77	321	12
83 - 30	Rim	6.32	0.89	1694	67	486 000	1500 0	2.65	0.24	70.3	9.8	19.8	1.2	17.1	1.4	2.9	0.3	145. 0	7.7	538	19	102	3	111 30	340	421	23	795	30
83 - 44	Rim	7.23	0.67	970	130	450 000	1400 0	0.72	0.22	118. 0	37.0	13.7	4.3	18.4	5.3	3.3	1.1	107. 0	20.0	250	21	45	3	102 30	220	195	16	308	21
83 - 46	Rim (i)	12.5 1	1.80	1780	100	536 000	1600 0	3.85	0.23	303. 0	20.0	41.1	6.0	44.9	6.4	7.7	1.1	179. 4	7.8	358	16	64	4	109 90	690	248	21	502	26

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-83 (aplitic syenite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
83 - 41	Core	9.91	0.98	2495	77	5040 00	1800 0	5.58	0.41	328.0	13.0	63.1	4.2	57.0	3.1	9.4	0.9	238.9	5.1	512	11	90	3	9350	360	545	24	419	16
83 - 72	Core	8.75	1.00	1187	54	5131 00	9700	0.80	0.08	296.0	8.2	15.6	1.3	19.9	1.2	3.7	0.4	121.3	7.8	266	12	49	3	1082 0	320	238	10	139	5
83 - 73	Core	33.53	3.50	5420	530	4962 00	6700	10.39	0.86	1550. 0	160.0	148.0	13.0	161.0	16.0	27.5	3.0	603.0	52.0	1226	66	210	10	1115 0	320	768	45	1952	67
83 - 5	Core	114. 79	5.90	127 30	800	451 300	740 0	29.5 0	2.30	528 0.0	370. 0	433. 0	31.0	507. 0	34.0	91.2	6.9	181 0.0	150. 0	223 0	160	361	22	101 80	180	326 0	240	184 3	80
83 - 8	Core	7.05	1.10	1122	54	4890 00	1300 0	0.21	0.02	112.9	8.7	5.3	0.3	8.3	0.6	1.4	0.1	110.5	7.7	284	10	52	2	9250	340	286	13	112	5
83 - 9	Core	37.41	1.70	1310 0	1500	4650 00	1000 0	27.60	3.20	5870. 0	770.0	410.0	37.0	507.0	52.0	99.0	10.0	1770. 0	200.0	1740	170	267	29	1193 0	330	1840	170	1390	68
83 - 12	Core	39.60	3.70	1120 0	1100	4950 00	1400 0	16.00	1.90	2910. 0	440.0	227.0	22.0	317.0	29.0	61.0	6.2	1700. 0	170.0	1810	140	270	18	8400	340	695	58	1640	160
83 - 18	Core	9.85	0.64	4950	110	4640 00	1600 0	17.46	0.79	726.0	69.0	162.0	5.8	165.4	8.8	28.5	1.5	577.0	22.0	1169	31	215	6	1291 0	380	988	39	2750	110
83 - 23	Core	15.21	0.90	9260	330	4883 00	7700	26.20	1.30	2950. 0	160.0	441.0	34.0	466.0	20.0	88.2	4.1	1262. 0	45.0	1275	39	197	5	1020 0	230	1272	78	1060	110
83 - 27	Core	19.80	7.50	2600	200	4730 00	8300	10.60	2.10	276.0	20.0	95.0	12.0	93.0	12.0	16.1	2.2	300.0	23.0	492	63	84	10	1021 0	290	430	64	697	69
83 - 31	Core	12.95	0.75	9000	1100	4769 00	8000	20.50	2.60	2300. 0	460.0	294.0	39.0	346.0	50.0	60.3	9.2	1200. 0	190.0	1530	130	246	19	1060 0	230	3020	320	2077	41
83 - 33	Core	25.14	1.70	6480	310	4550 00	1400 0	13.29	0.66	2250. 0	130.0	190.4	9.5	217.0	11.0	37.5	1.9	788.0	45.0	1320	47	221	10	1001 0	260	1820	170	1355	85
83 - 39	Core	30.97	1.20	3520	130	4330 00	1700 0	7.65	0.25	141.8	4.7	82.4	3.5	72.1	2.7	14.6	0.6	373.0	14.0	661	18	122	4	8190	440	315	9	567	13
83 - 43	Core	8.50	0.71	1150	120	4110 00	1100 0	0.55	0.05	99.8	4.1	11.6	1.0	18.2	3.0	3.1	0.2	120.1	6.7	262	19	47	2	8110	270	253	12	213	7
83 - 48	Core	11.54	1.10	3910	120	4360 00	1300 0	5.72	0.60	246.0	20.0	93.3	8.5	85.8	6.9	14.6	1.3	395.0	15.0	950	31	164	6	9600	250	1303	73	1220	110

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-83 (aplitic syenite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
83 - 52	Core	21.99	1.30	3620	170	4367 00	9000	8.04	0.47	793.0	46.0	123.4	8.0	148.1	8.5	26.7	1.8	525.0	31.0	675	32	105	4	9430	210	3020	140	551	20
83 - 58	Core	5.00	0.43	2965	98	4920 00	1400 0	2.61	0.37	122.0	11.0	35.7	3.6	40.9	3.3	6.7	0.5	284.0	10.0	845	32	149	6	1065 0	350	870	37	1521	68
83 - 54	Core	13.73	1.10	3530	160	4990 00	1100 0	7.80	1.10	749.0	92.0	97.0	7.4	104.5	7.3	18.4	1.5	369.0	17.0	772	43	132	6	1139 0	430	1390	100	900	100
83 - 60	Core	18.23	0.92	2460 0	1200	4210 00	1200 0	25.90	1.30	743.0	48.0	334.0	18.0	512.0	25.0	121.4	6.8	3730. 0	220.0	3310	150	483	20	1054 0	240	6670	840	774	84
83 - 63	Core	39.96	3.00	4260	180	4490 00	1400 0	8.43	0.43	821.0	23.0	143.2	7.5	157.8	6.4	27.3	1.2	535.0	30.0	810	45	143	7	8610	270	687	34	750	31
83 - 68	Core	5.31	0.53	2823	53	4920 00	1400 0	4.76	0.16	280.0	11.0	40.8	2.5	42.5	1.7	6.5	0.3	284.7	9.0	813	23	145	4	1086 0	340	671	23	1418	47
83 - 70	Core	42.15	2.30	6790	240	4940 00	1400 0	16.17	0.58	2421. 0	65.0	250.0	10.0	310.0	11.0	56.2	2.8	1004. 0	47.0	1115	52	166	6	1027 0	230	1976	88	930	31
83 - 2	Rim	16.76	1.60	6490	580	4680 00	1300 0	33.90	2.10	990.0	130.0	219.0	19.0	226.0	27.0	44.3	5.4	827.0	96.0	1270	60	210	10	1145 0	260	1622	82	2759	65
83 - 4	Rim	8.95	0.74	3080	120	4580 00	1300 0	23.80	0.74	252.0	17.0	102.8	5.1	78.0	4.1	16.0	0.7	325.0	15.0	787	37	141	5	1089 0	270	1019	26	2183	56
83 - 6	Rim (i1)	36.20	2.90	4350	180	4730 00	1600 0	8.67	0.61	1910. 0	130.0	145.0	13.0	179.0	15.0	32.0	3.1	633.0	33.0	828	47	137	10	1074 0	840	1242	86	559	26
83 - 10	Rim	17.49	1.70	4690	240	4819 00	7500	29.50	1.00	920.0	120.0	169.0	13.0	125.0	15.0	23.0	3.0	478.0	43.0	1155	38	202	5	1112 0	220	1542	46	3135	66
83 - 15	Rim	35.47	2.90	4960	300	4666 00	6500	15.30	2.30	2160. 0	230.0	209.0	28.0	243.0	32.0	38.0	5.0	649.0	63.0	1040	49	173	7	1120 0	180	2070	110	1292	37
83 - 19	Rim	4.63	0.54	1572	91	4450 00	1000 0	3.25	0.46	128.0	34.0	26.3	3.2	27.6	4.5	5.2	0.8	146.0	14.0	465	12	89	2	1054 0	170	546	18	829	30
83 - 22	Rim	48.34	6.60	4430	180	4850 00	1500 0	32.30	2.20	672.0	56.0	169.0	14.0	135.7	9.9	25.6	1.5	459.0	20.0	1088	32	193	4	1184 0	280	1430	72	2905	80
83 - 26	Rim	162.7 7	28.00	2431	90	4610 00	1800 0	4.50	0.49	148.0	17.0	29.1	2.7	31.5	2.5	5.4	0.4	214.7	9.3	752	28	144	4	9970	340	595	26	1901	50

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-83 (aplitic syenite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
83 - 28	Rim	19.50	0.94	4490	150	4623 00	8800	22.20	1.60	620.0	55.0	136.9	4.9	133.0	8.0	23.5	1.4	537.0	24.0	998	31	170	5	1164 0	240	1582	71	1927	54
83 - 36	Rim	9.91	0.96	3230	99	4910 00	1100 0	5.82	0.32	532.0	48.0	71.5	5.7	76.0	4.6	13.2	0.7	321.0	19.0	816	36	149	9	1237 0	300	770	44	2104	85
83 - 38	Rim	126.3 3	20.00	3172	83	4710 00	1200 0	33.10	1.80	312.0	24.0	83.7	6.3	65.6	3.3	12.6	0.5	320.9	9.2	853	23	160	3	1176 0	310	1271	51	2834	66
83 - 51	Rim	21.99	2.50	3730	330	4720 00	1400 0	12.90	1.10	545.0	98.0	114.0	14.0	112.0	15.0	20.0	2.8	397.0	35.0	799	38	143	7	1076 0	370	1342	78	2209	54
83 - 61	Rim	21.14	1.80	5400	420	4911 00	8500	13.10	1.00	269.0	32.0	98.0	9.7	96.0	11.0	22.0	2.7	572.0	53.0	1335	59	242	7	1354 0	310	1297	82	2571	77
83 - 66	Rim	22.11	1.50	4900	370	4446 00	7700	3.91	0.85	130.0	17.0	48.6	6.4	76.2	9.4	17.8	1.9	625.0	54.0	781	55	114	7	9970	160	1080	150	648	28

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-83 (aplitic syenite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
91 - 10	Rim	8.28	0.63	915	16	4436 00	4400	0.61	0.06	20.3	0.4	2.9	0.3	3.7	0.2	0.4	0.0	77.2	1.4	279	5	53	1	9570	200	144	3	168	4
91 - 14	Rim (i)	9.62	0.70	820	17	4805 00	8400	0.02	0.01	28.1	0.5	1.1	0.1	2.7	0.2	0.3	0.1	66.8	2.7	246	7	47	1	9040	210	210	5	216	6
91 - 21	Rim	8.99	1.00	728	33	4232 00	8700	0.69	0.11	17.1	0.5	2.8	0.3	3.3	0.4	0.4	0.1	60.5	2.6	253	14	50	2	9580	220	207	4	328	13
91 - 35	Rim	14.70	1.80	636	14	4230 00	1300 0	5.60	4.70	35.0	12.0	7.1	5.2	3.4	1.0	0.4	0.1	59.6	1.7	207	5	40	1	9230	210	160	3	197	4
91 - 37	Rim	5.82	0.52	825	20	4302 00	8800	7.06	0.85	41.3	1.8	13.5	1.1	5.8	0.4	0.7	0.1	72.9	2.3	255	6	49	1	9390	220	197	5	251	5
91 - 46	Rim	5.64	0.42	829	23	4434 00	8100	0.11	0.03	22.5	0.5	1.3	0.2	2.7	0.2	0.2	0.0	68.8	2.5	257	10	50	2	9750	230	263	7	317	12
91 - 64	Rim	8.81	0.68	806	35	4850 00	2200 0	0.08	0.02	23.6	1.0	1.4	0.3	3.3	0.3	0.3	0.1	69.1	3.8	246	8	47	2	1017 0	300	210	10	248	11
91 - 28	Rim	7.88	0.73	677	13	4757 00	8300	0.02	0.00	18.0	0.3	1.0	0.1	2.3	0.2	0.2	0.0	55.6	1.3	208	6	40	1	9310	270	110	2	119	3
91 - 24	Core	14.61	0.57	1559	50	4620 00	1100 0	9.53	0.57	36.6	1.5	19.7	1.3	11.3	0.6	1.1	0.1	135.5	4.6	348	11	66	2	8120	260	161	8	134	6
91 - 43	Core	12.51	1.20	621	67	4531 00	6900	14.70	6.30	43.0	15.0	21.9	8.9	6.9	2.0	0.5	0.1	56.2	7.0	172	18	33	3	8010	140	47	5	63	5
91 - 47	Core	14.41	0.90	1852	60	5000 00	1200 0	1.30	0.54	22.0	1.5	9.8	1.0	10.8	0.8	1.5	0.1	160.8	8.5	432	25	79	4	8530	200	201	11	181	6
91 - 49	Core	7.34	0.69	1685	33	4682 00	8200	0.62	0.12	30.4	0.7	5.0	0.4	6.9	0.3	0.7	0.1	136.8	3.3	459	12	86	2	9670	220	343	12	324	11
91 - 54	Core	4.35	0.80	606	39	4450 00	1300 0	0.04	0.01	15.4	0.6	0.8	0.1	1.8	0.3	0.1	0.0	48.2	3.4	196	13	39	3	9530	250	144	11	213	10
91 - 63	Core	8.28	0.61	790	22	4373 00	8100	0.01	0.00	10.7	0.3	1.5	0.2	3.1	0.2	0.3	0.0	68.1	2.0	237	5	46	1	8900	170	79	3	94	3
91 - 65	Core	3.78	0.47	555	15	4810 00	8000	0.18	0.05	9.9	0.3	1.3	0.2	2.1	0.2	0.2	0.0	45.9	1.4	173	8	34	1	1004 0	150	57	2	191	8

Spot #	Obs Core/ Rim	Ті	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
91 - 4	Rim	6.45	0.54	766	33	4800 00	1400 0	0.01	0.01	25.8	0.8	1.0	0.1	2.6	0.2	0.2	0.0	65.3	2.5	232	7	44	1	1002 0	220	216	6	254	9
91 - 8	Rim	3.89	0.46	411	14	4160 00	1000 0	0.01	0.00	10.8	0.4	0.4	0.1	0.9	0.1	0.1	0.0	33.1	1.6	159	4	33	1	1017 0	260	102	4	180	7
91 - 15	Rim (o)	6.88	0.98	854	39	4710 00	1400 0	9.50	3.60	46.6	8.0	14.3	5.4	5.2	1.5	0.3	0.1	67.2	3.7	250	6	48	2	9730	240	250	7	301	7
91 - 23	Rim	6.15	0.51	624	47	4400 00	1400 0	0.30	0.12	17.5	1.1	1.7	0.4	2.4	0.3	0.4	0.1	54.9	4.1	201	12	39	2	9540	230	103	6	146	7
91 - 25	Rim (i)	8.33	0.89	1183	32	4440 00	1100 0	0.36	0.10	22.1	1.2	3.1	0.5	5.0	0.5	0.5	0.1	105.1	5.4	339	12	65	2	9430	230	230	11	235	9
91 - 30	Rim	4.64	0.51	646	18	4100 00	1000 0	0.01	0.01	12.2	0.3	0.4	0.1	1.7	0.2	0.2	0.0	63.6	2.8	184	8	37	1	8780	220	58	3	166	6
91 - 48	Rim	5.13	0.47	800	21	4470 00	1000 0	0.06	0.03	21.6	1.4	1.4	0.2	2.7	0.3	0.2	0.0	67.2	2.7	283	8	53	1	1020 0	120	270	9	373	12
91 - 66	Rim	6.67	0.85	1108	49	4390 00	1100 0	0.88	0.14	14.4	1.1	6.7	0.7	7.1	0.6	1.0	0.1	110.7	6.7	293	12	55	2	9200	200	125	7	255	6
91 - 29	Core	5.19	0.47	982	37	4314 00	8800	0.02	0.01	11.6	0.4	1.2	0.1	3.1	0.3	0.2	0.0	86.4	3.5	276	11	52	2	1016 0	200	106	5	339	9
91 - 40	Core	15.91	1.10	3480	230	3970 00	1400 0	0.86	0.19	21.8	0.9	11.9	0.6	18.5	2.1	2.6	0.3	316.0	18.0	819	60	149	9	6670	280	599	47	361	22
91 - 22	Core	15.79	1.30	3400	130	4690 00	1100 0	14.70	4.10	98.0	12.0	48.0	8.2	30.9	3.6	7.3	0.6	302.0	19.0	1065	28	204	5	9780	280	1337	89	2598	68
91 - 68	Core	6.62	0.68	592	17	4120 00	1100 0	0.20	0.02	16.0	0.6	1.5	0.2	2.0	0.3	0.1	0.0	51.8	2.2	201	4	40	2	8940	270	108	3	152	4
91 - 69	Core	19.92	2.10	1397	46	4090 00	1000 0	1.85	0.13	30.6	1.6	8.8	1.0	8.6	0.6	1.2	0.1	129.7	5.9	414	20	75	2	9180	290	264	15	235	7
91 - 70	Rim	35.7 1	2.80	238 3	52	482 000	160 00	9.20	0.68	71.7	2.7	34.0	2.0	22.2	2.0	4.5	0.3	247. 0	16.0	792	38	133	6	108 80	600	494	52	594	42
91 - 1	Core	7.41	1.70	892	15	4660 00	2400 0	0.09	0.03	25.1	1.2	1.7	0.3	3.6	0.2	0.2	0.1	84.4	5.1	275	14	51	3	1066 0	730	239	11	293	17

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-91 (syenite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
91 - 2	Rim	19.92	1.30	1055	29	4583 00	7800	1.72	0.21	29.5	1.2	7.1	0.7	6.3	0.4	1.0	0.1	100.0	4.1	339	13	62	2	8970	160	223	10	210	7
91 - 6	Rim	9.81	0.85	1129	48	4520 00	1100 0	1.50	0.25	36.2	1.7	6.4	0.9	6.0	0.5	0.9	0.1	99.9	4.4	337	13	63	2	9770	210	439	15	458	9
91 - 7	Core	11.54	1.20	1180	77	4100 00	1100 0	2.96	0.20	20.9	0.9	8.7	0.7	5.0	0.6	0.8	0.1	77.9	7.2	513	21	105	4	6420	160	244	5	324	9
91 - 9	Core	39.11	3.30	1910	510	4220 00	1000 0	1.04	0.09	11.9	0.5	9.2	2.4	18.6	6.5	7.8	3.1	237.0	85.0	359	68	66	10	8210	250	80	7	129	7
91 - 11	Core	17.37	1.20	511	17	4496 00	8500	9.80	0.61	52.0	1.5	32.0	1.9	10.0	0.7	3.1	0.2	50.0	1.5	142	4	27	1	9160	220	40	1	73	3
91 - 13	Core	10.20	1.80	1265	64	4311 00	4200	1.21	0.53	19.9	2.4	6.1	1.9	6.6	1.3	1.1	0.2	120.1	6.2	366	20	68	2	9900	340	154	5	355	25
91 - 19	Rim	24.05	1.20	1033	37	4580 00	2000 0	2.60	0.11	31.7	1.2	10.9	0.5	8.2	0.4	1.4	0.1	103.7	2.7	325	22	59	4	9250	700	204	27	214	28
91 - 20	Core	16.64	1.10	650	49	4490 00	1500 0	0.53	0.15	12.8	1.1	2.8	0.5	3.8	0.5	0.7	0.1	62.7	3.8	205	13	38	2	7850	210	79	5	103	7
91 - 27	Core	6.83	0.51	565	13	4610 00	1100 0	0.89	0.10	19.2	0.6	3.1	0.4	2.7	0.3	0.5	0.0	49.1	1.4	181	6	35	1	1016 0	330	114	3	165	5
91 - 31	Core	52.84	3.30	3392	82	4940 00	2200 0	11.25	0.55	82.5	4.1	46.5	3.0	32.1	1.2	5.6	0.3	349.0	12.0	1085	59	187	2	1094 0	600	996	43	1106	80
91 - 32	Rim (i)	28.79	1.60	1740	57	4349 00	7400	6.81	0.50	55.4	3.1	27.4	1.8	16.3	0.9	3.8	0.2	177.9	7.3	632	25	120	4	9430	190	288	9	443	9
91 - 33	Rim (o)	13.26	0.71	916	42	4300 00	1100 0	1.25	0.12	30.2	1.5	5.8	0.5	5.0	0.4	0.6	0.1	85.7	4.6	307	13	56	2	9270	160	207	11	247	12
91 - 34	Core	11.95	0.91	373	18	4116 00	9500	0.48	0.04	11.4	0.3	1.6	0.2	1.4	0.2	0.2	0.0	30.8	1.3	131	5	26	1	8320	240	58	1	62	2
91 - 36	Core	12.88	1.40	1300	130	4148 00	6600	1.47	0.22	16.7	1.1	9.2	1.0	9.5	1.0	2.0	0.3	118.0	12.0	360	47	77	12	8910	260	127	12	178	8
91 - 38	Core	17.73	1.60	1541	64	5140 00	2000 0	1.36	0.18	11.3	0.7	6.9	0.5	8.4	0.7	0.9	0.1	129.1	6.3	408	15	78	2	8560	290	125	11	321	15

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-91 (syenite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
91 - 39	Rim	30.0 0	2.10	129 1	37	464 700	840 0	3.39	0.17	40.8	1.3	14.7	0.8	9.6	0.6	1.9	0.1	124. 9	6.0	424	8	76	3	107 70	340	288	8	412	15
91 - 42	Rim (o)	12.51	1.40	887	58	4375 00	7900	2.37	0.30	23.3	2.4	9.1	1.4	6.6	0.9	1.3	0.2	83.8	7.7	338	21	62	3	1002 0	150	145	4	265	7
91 - 44	Rim	27.69	2.10	665	23	4520 00	1400 0	1.27	0.13	22.9	1.5	5.9	0.5	6.5	0.8	1.5	0.3	75.5	3.9	206	11	38	2	9750	330	145	11	177	13
91 - 45	Core	8.84	0.77	562	13	4600 00	1000 0	0.99	0.09	18.9	0.6	3.6	0.3	2.7	0.3	0.4	0.0	46.4	1.3	187	6	38	1	9330	230	95	2	136	3
91 - 52	Core	25.39	1.30	1371	90	4460 00	1000 0	2.16	0.22	29.2	1.5	11.3	1.3	9.3	0.9	1.5	0.2	140.0	10.0	394	21	72	3	8550	180	193	11	221	13
91 - 53	Rim	9.40	0.70	433	11	4050 00	7500	2.35	0.80	16.6	1.6	2.6	0.7	1.8	0.2	0.2	0.0	37.5	1.3	141	4	28	1	8500	150	68	2	86	2
91 - 55	Rim	25.51	2.60	844	35	4430 00	1100 0	2.63	0.23	23.4	1.1	9.7	0.9	5.9	0.5	1.5	0.1	74.8	3.6	350	16	74	3	1105 0	280	258	7	596	17
91 - 56	Core	13.00	1.30	4080	190	4758 00	8500	13.52	0.87	37.6	3.3	16.1	2.2	12.5	1.0	2.1	0.3	328.0	17.0	1352	65	233	12	1144 0	310	1530	110	3290	220
91 - 57	Rim	17.86	5 1.70	1530	190	4390 00	1400 0	5.80	1.30	44.2	6.1	17.6	3.3	12.4	2.0	2.9	0.7	144.0	18.0	448	38	82	6	1004 0	240	446	54	633	51

Spot #	Obs Core/ Rim	Ті	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
136 - 1	Core	12.03	1.30	1438	40	5180 00	2600 0	1.04	0.09	53.4	3.4	13.2	1.2	11.8	0.7	2.9	0.3	143.6	6.2	415	10	76	3	1003 0	280	332	18	253	9
136 - 6	Core	5.45	0.58	629	14	4790 00	1300 0	0.02	0.01	15.3	0.5	0.9	0.1	2.5	0.2	0.1	0.0	61.4	2.0	219	7	42	1	9970	280	126	6	172	9
136 - 11	Core	9.12	0.79	754	47	4924 00	9200	0.08	0.02	22.1	1.6	2.1	0.4	3.6	0.4	0.4	0.1	70.5	5.0	245	12	47	3	9130	230	167	13	182	11
136 - 13	Core	13.12	1.20	1596	78	4380 00	1800 0	1.51	0.14	46.1	1.7	13.1	1.4	11.6	1.3	2.4	0.4	143.3	7.4	432	14	81	3	8540	250	524	31	449	15
136 - 24	Core	11.42	1.50	3410	230	4520 00	6700	0.85	0.23	49.3	1.9	18.8	1.6	22.7	1.2	2.5	0.4	310.0	18.0	814	56	145	9	7820	260	729	75	347	25
136 - 26	Core	9.11	0.71	928	29	5290 00	1300 0	2.78	0.30	26.7	1.1	6.3	0.5	6.1	0.6	1.1	0.1	83.5	3.3	268	10	49	2	1143 0	420	296	10	341	9
136 - 30	Core	19.19	1.10	1610	180	4758 00	8100	2.75	0.24	50.4	6.2	20.4	1.9	17.4	1.8	3.4	0.3	161.0	17.0	499	51	93	11	9300	170	427	80	421	46
136 - 40	Core	9.60	0.72	1084	76	4620 00	1700 0	16.60	5.90	58.0	14.0	25.6	8.3	9.3	1.7	0.6	0.1	103.9	5.4	309	14	61	3	9720	200	169	8	191	5
136 - 42	Core	9.86	0.72	3240	95	4520 00	1300 0	0.14	0.03	37.2	1.0	15.5	0.5	23.9	1.0	1.6	0.1	331.0	12.0	745	26	132	5	8050	170	708	34	458	13
136 - 44	Core	20.04	1.50	3690	220	4954 00	8100	3.92	0.35	142.5	9.1	31.9	3.0	30.7	2.2	4.8	0.6	353.0	24.0	970	57	164	10	8370	170	2650	220	1110	54
136 - 46	Core	11.42	1.40	1370	110	4320 00	1200 0	1.86	0.37	31.9	3.3	13.8	2.5	12.6	1.9	3.9	0.7	138.0	14.0	387	19	68	3	1005 0	230	301	10	419	12
136 - 56	Rim	5.04	0.57	403	17	4540 00	1400 0	0.40	0.09	14.5	0.9	1.7	0.4	2.1	0.3	0.3	0.1	39.6	2.4	143	5	28	1	1027 0	200	102	5	157	4
136 - 2	Rim (i)	11.66	1.20	1068	48	5240 00	1300 0	1.37	0.32	45.4	4.0	14.0	3.4	12.1	2.2	3.2	0.7	100.9	7.1	270	9	49	1	1037 0	380	294	13	320	15
136 - 3	Rim (o)	8.62	1.10	108 9	44	510 000	120 00	1.52	0.23	43.6	2.6	16.1	2.7	12.8	2.3	4.1	0.7	102. 5	5.9	372	13	81	4	137 60	540	408	53	636	61
136 - 5	Rim	26.6 0	4.40	143 0	100	450 800	890 0	10.4 0	2.20	57.0	7.5	29.8	5.1	18.2	2.8	5.2	0.9	156. 0	15.0	476	34	79	5	109 90	270	336	13	623	30

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
136 - 7	Rim	12.05	0.96	1459	43	4620 00	8900	1.79	0.11	39.0	1.0	17.2	1.1	16.2	0.8	4.7	0.2	152.2	4.7	345	9	61	2	9600	280	289	7	279	5
136 - 17	Rim (o)	20.16	1.60	648	21	4798 00	8900	0.70	0.10	11.8	0.8	3.4	0.6	2.7	0.4	0.6	0.1	47.6	2.6	280	9	63	2	1232 0	270	208	6	553	14
136 - 21	Rim	11.05	1.30	1580	150	4550 00	9900	11.60	2.30	62.3	9.6	37.5	5.7	20.5	2.8	17.9	3.2	151.0	16.0	633	55	120	10	1324 0	360	298	18	1020	120
136 - 23	Rim	11.78	1.10	567	15	4150 00	1100 0	0.47	0.05	22.0	0.6	4.3	0.8	4.1	0.4	0.9	0.1	57.3	2.3	179	5	34	1	8730	230	172	10	184	8
136 - 27	Rim	6.22	0.60	631	43	4807 00	8200	2.11	0.25	18.7	1.3	4.5	0.8	3.8	0.6	0.7	0.1	56.4	4.0	212	14	41	3	1104 0	220	146	8	247	8
136 - 29	Rim	2.94	0.45	772	23	4640 00	1300 0	0.04	0.02	13.7	0.3	0.7	0.1	1.9	0.2	0.1	0.0	59.8	2.4	308	12	62	3	1168 0	420	318	11	524	27
136 - 31	Rim	9.58	0.69	629	19	4657 00	8900	0.25	0.03	19.6	0.6	3.0	0.3	3.4	0.3	0.6	0.1	61.9	2.1	215	6	40	1	9960	250	148	6	186	6
136 - 36	Rim	15.31	1.10	1170	22	4724 00	8200	1.64	0.08	37.7	0.7	14.5	0.8	11.4	0.5	2.7	0.2	107.4	2.5	363	7	67	1	1012 0	190	269	8	341	7
136 - 38	Rim (i)	27.94	3.20	3397	94	5380 00	2200 0	4.46	0.30	80.8	1.7	44.8	2.9	42.3	2.2	8.8	0.6	340.1	6.9	797	22	139	7	9630	440	764	30	490	12
136 - 39	Rim (o)	8.21	0.63	600	9	4539 00	6300	0.54	0.28	22.0	0.6	1.5	0.3	2.3	0.2	0.2	0.0	53.4	1.3	192	4	37	1	9150	210	141	3	158	3
136 - 43	Rim	6.92	0.66	635	25	4810 00	1500 0	0.02	0.01	23.0	0.6	1.0	0.1	2.2	0.2	0.2	0.0	60.0	2.1	217	6	42	1	9810	260	144	4	169	4
136 - 52	Rim (o)	7.09	0.69	1029	46	4800 00	1000 0	10.20	3.50	52.5	6.0	19.3	4.0	9.3	0.5	1.2	0.2	98.1	6.8	330	17	60	2	1073 0	290	257	11	309	10
136 - 57	Rim	5.37	0.64	730	27	4510 00	1200 0	25.00	19.00	79.0	43.0	34.0	25.0	8.1	4.2	0.3	0.1	60.6	2.7	216	7	44	1	9450	260	196	6	245	7
136 - 60	Rim	16.52	1.50	1957	45	4557 00	5300	3.09	0.16	41.4	1.7	19.9	1.2	17.0	1.1	4.3	0.3	184.1	7.7	556	16	100	3	1009 0	190	417	11	473	14
136 - 62	Rim	6.88	0.96	854	43	4153 00	9700	14.70	9.90	59.0	27.0	28.0	16.0	9.7	3.4	1.0	0.2	83.2	5.5	279	11	53	2	9580	210	262	7	335	7

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
136 - 64	Rim	10.20	1.00	871	49	4181 00	7100	16.30	2.60	62.3	6.8	24.7	4.5	10.0	1.5	1.1	0.2	81.9	6.5	259	12	50	2	8840	150	204	7	219	6
136 - 66	Rim	9.47	0.74	897	21	4386 00	7700	0.92	0.05	26.9	0.9	7.4	0.6	7.7	0.4	1.5	0.1	96.7	3.4	271	9	49	1	9760	210	250	9	212	8
136 - 10	Core	12.40	0.83	1280	140	4960 00	1000 0	3.30	2.30	34.2	7.6	13.1	4.6	11.5	2.0	2.4	0.2	119.0	15.0	354	37	63	6	9990	270	241	26	188	7
136 - 20	Core	21.38	1.10	1869	65	4477 00	7100	2.93	0.30	47.3	2.5	23.3	2.3	18.4	1.4	3.9	0.5	182.6	9.2	535	25	98	3	9740	200	518	22	520	16
136 - 25	Rim	30.97	1.90	2403	98	4576 00	9000	15.11	0.80	115.5	3.0	57.2	2.4	35.8	2.4	24.2	1.4	257.0	12.0	631	17	105	3	9310	230	1084	46	786	21
136 - 33	Rim	28.18	4.10	1690	190	3910 00	2300 0	10.10	1.40	79.3	9.7	52.9	8.6	33.3	5.1	21.0	2.5	186.0	24.0	564	63	114	11	9290	440	226	27	780	82
136 - 53	Core	33.65	5.50	2060	610	4930 00	2200 0	3.90	1.80	57.0	22.0	40.0	18.0	31.0	13.0	6.9	3.0	230.0	74.0	580	170	99	28	9330	400	380	150	308	97
136 - 54	Rim (i)	13.36	1.00	1169	44	4480 00	1200 0	0.77	0.08	22.3	0.5	7.3	0.5	8.5	0.4	1.6	0.1	113.2	4.5	323	10	61	2	8420	360	177	8	142	6
136 - 4	Core	51.8 7	4.40	376 0	400	458 000	160 00	17.4 0	2.00	145. 0	19.0	101. 0	13.0	71.4	9.5	18.7	2.6	454. 0	49.0	111 9	82	186	14	100 20	210	130 0	220	106 0	120
136 - 28	Core	90.62	4.30	1506	50	4970 00	1400 0	2.74	0.16	29.7	0.9	15.5	0.5	14.3	1.0	3.0	0.2	145.6	4.6	393	12	72	2	7620	250	227	7	183	4
136 - 34	Core (i)	119.0 4	25.00	1000	120	4450 00	1000 0	1.23	0.38	24.4	1.5	9.8	1.3	9.6	1.4	2.5	0.4	99.0	14.0	282	33	52	6	8160	200	93	11	82	8
136 - 50	Core	32.80	2.80	3310	230	4001 00	9200	7.22	0.65	81.8	7.7	61.3	6.6	51.6	5.4	12.0	1.1	377.0	36.0	815	87	133	13	7660	220	296	40	275	26
136 - 61	Core	47.13	3.70	3850	240	4600 00	1200 0	12.90	1.50	105.0	9.2	53.4	6.3	40.3	4.4	17.7	2.1	379.0	31.0	1072	77	175	11	9490	360	1262	54	1322	39
136 - 9	Rim	33.04	4.30	2840	300	4730 00	1300 0	16.00	8.30	85.0	20.0	48.8	9.8	37.0	6.1	7.4	1.0	303.0	35.0	930	110	152	16	1143 0	310	860	100	1240	130
136 - 19	Rim	218.6 4	55.00	958	83	3020 00	2800 0	2.80	0.30	21.1	1.6	14.8	1.6	9.9	1.1	3.3	0.4	85.1	8.7	452	41	94	9	9080	880	165	19	709	59

LA-ICP-MS trace-element measurements in zircon grains for sample USP14-136 (monzonite)

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
136 - 47	Rim	46.77	2.80	2703	64	4520 00	1200 0	25.40	1.10	144.0	5.4	102.2	3.9	51.3	2.2	31.7	1.4	284.4	8.8	684	13	129	3	1350 0	250	439	13	1108	44
136 - 37	Core	8.64	0.77	1409	84	4540 00	1300 0	0.35	0.07	27.2	1.4	6.2	0.7	8.7	0.9	1.0	0.1	130.7	9.0	340	20	65	3	8510	190	201	12	181	11
136 - 18	Core	18.77	0.90	2510	230	4680 00	1400 0	2.60	0.23	86.4	9.2	23.8	1.6	22.3	1.1	4.2	0.4	258.0	24.0	690	49	120	8	8610	140	960	160	615	65
136 - 32	Core	12.63	0.91	738	47	5010 00	1500 0	0.34	0.06	16.1	0.7	3.1	0.4	4.8	0.4	0.8	0.1	69.7	4.3	216	10	41	2	9770	240	102	3	137	4
136 - 35	Core (o)	22.23	1.60	918	57	5210 00	1400 0	0.88	0.11	33.0	1.6	8.2	0.8	7.8	0.6	2.1	0.2	87.1	4.6	266	11	50	2	8350	180	111	3	101	4
136 - 65	Core	16.52	2.40	3190	950	4470 00	1500 0	2.52	0.34	78.0	23.0	26.6	6.8	29.4	8.8	5.9	1.9	330.0	100.0	820	220	146	37	7440	370	980	330	460	100

Spot #	Obs Core/ Rim	Ті	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
144 - 5	Core	8.02	0.99	1152	84	4400 00	1100 0	36.20	2.40	124.9	7.0	63.9	3.0	17.3	1.3	5.9	0.4	104.4	6.7	278	14	54	3	8450	230	161	11	135	10
144 - 21	Core	13.36	1.50	5930	170	4930 00	1600 0	5.64	0.64	132.0	11.0	36.8	3.1	25.1	1.5	1.4	0.2	519.0	16.0	1891	36	331	6	1264 0	380	4681	91	7260	200
144 - 26	Core	9.47	1.60	750	33	4780 00	1300 0	4.60	2.20	127.0	42.0	7.1	1.2	1.7	0.2	0.1	0.0	38.5	1.3	441	32	106	6	9630	310	232	37	1343	82
144 - 35	Core	6.44	0.66	1203	22	4632 00	5700	21.00	10.00	60.0	16.0	11.1	4.6	5.1	0.7	0.7	0.3	96.2	2.3	344	9	66	1	1042 0	190	404	8	476	8
144 - 42	Core	7.34	0.73	1461	50	4360 00	1100 0	3.02	0.91	28.3	2.6	11.4	2.2	8.8	0.9	0.5	0.1	124.5	5.1	425	16	80	2	1026 0	220	383	16	437	15
144 - 46	Core	8.14	1.10	1650	130	4110 00	1300 0	17.90	6.90	42.0	8.7	11.4	4.9	6.3	1.2	0.7	0.4	130.3	7.8	491	39	90	6	9620	510	920	110	1710	150
144 - 51	Core	11.64	0.97	2092	94	4830 00	1500 0	40.40	2.80	152.0	10.0	87.0	11.0	29.8	2.7	4.0	0.5	207.0	11.0	578	34	97	4	1143 0	320	1253	99	1110	66
144 - 57	Core	6.30	0.65	611	27	4781 00	7500	2.31	0.30	22.6	0.7	8.7	0.6	4.3	0.2	0.7	0.1	52.5	2.8	187	5	36	1	1060 0	270	133	5	185	3
144 - 64	Core	15.18	2.80	4670	170	4610 00	8200	39.00	11.00	78.0	30.0	33.0	16.0	12.5	3.6	0.5	0.2	361.0	24.0	1654	60	301	8	1332 0	430	2990	530	5570	430
144 - 67	Core	9.21	0.74	353	8	4380 00	7700	18.50	1.70	35.2	2.3	18.6	1.3	6.2	0.4	6.8	0.7	31.4	1.2	117	4	24	1	1013 0	240	68	1	120	2
144 - 69	Core	3.04	1.10	2950	140	4790 00	1600 0	20.10	7.90	39.4	7.6	3.9	0.9	7.5	0.5	0.3	0.1	217.0	15.0	837	79	146	11	1133 0	290	1190	110	1420	150
144 - 71	Core	7.62	0.97	1295	52	4660 00	1700 0	29.30	8.00	89.0	19.0	33.9	7.4	8.7	0.9	1.1	0.2	114.2	5.7	391	19	75	3	1115 0	330	347	21	490	26
144 - 79	Core	20.41	3.00	3430	660	4570 00	1100 0	34.00	10.00	136.0	38.0	74.0	27.0	25.5	8.1	0.8	0.2	259.0	55.0	1010	100	196	19	1115 0	220	1120 0	3300	9200	2200
144 - 6	Rim	5.58	0.89	1954	70	4910 00	1100 0	43.00	11.00	100.0	13.0	24.2	2.7	8.9	0.6	5.7	1.4	148.8	6.3	652	35	123	5	1129 0	230	716	48	1033	28
144 - 8	Rim	14.70	1.20	1294	45	4650 00	1700 0	26.00	4.70	65.5	8.1	35.1	7.4	11.4	1.8	2.0	0.4	94.7	3.3	531	19	110	4	1357 0	430	337	9	1600	44

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
144 - 10	Rim	14.09	1.60	848	55	4812 00	7900	16.70	5.50	67.0	16.0	41.0	12.0	17.0	4.3	1.3	0.3	73.8	6.1	254	15	49	2	1012 0	250	172	10	224	10
144 - 13	Rim (o)	2.43	0.33	1298	30	4495 00	8900	10.00	4.60	25.9	5.3	3.7	1.5	3.2	0.3	0.2	0.1	98.1	3.3	479	14	92	3	1202 0	310	549	10	1045	46
144 - 24	Rim	6.50	0.49	688	12	4449 00	7300	0.01	0.01	23.6	0.5	1.0	0.1	2.4	0.2	0.2	0.0	59.9	1.6	216	6	42	1	1000 0	210	173	4	206	4
144 - 25	Rim	9.47	1.10	730	26	4980 00	2000 0	0.04	0.01	24.1	1.2	1.6	0.2	3.2	0.4	0.5	0.1	72.5	3.8	232	13	44	2	1009 0	470	134	9	156	10
144 - 30	Rim	4.30	0.41	1059	29	4490 00	1300 0	12.80	3.60	36.9	4.3	4.6	0.6	4.2	0.3	0.4	0.0	86.0	2.7	370	10	74	2	1051 0	280	518	17	625	27
144 - 34	Rim	7.48	0.62	682	28	4220 00	1100 0	12.50	2.70	92.0	14.0	67.0	11.0	17.7	2.9	10.9	1.5	67.3	3.7	211	8	42	1	9110	220	168	10	203	14
144 - 38	Rim (i)	12.63	1.70	722	11	3992 00	7300	29.60	1.50	95.1	3.1	49.7	1.9	12.6	0.7	4.2	0.4	67.7	2.6	223	6	43	2	8640	300	183	4	202	5
144 - 41	Rim	4.51	0.47	1010	31	4500 00	1300 0	12.30	3.70	50.0	10.0	16.6	5.4	4.7	0.8	2.2	0.8	80.6	2.3	365	9	72	1	1087 0	200	356	13	595	20
144 - 52	Rim	7.32	0.48	796	13	4406 00	8200	2.70	1.80	31.1	5.8	8.9	4.3	5.2	1.0	0.5	0.1	71.5	2.1	245	5	48	1	9120	180	193	3	204	3
144 - 54	Rim	3.75	0.68	824	23	4470 00	1000 0	9.10	4.60	30.4	9.1	11.7	5.3	4.8	1.5	0.6	0.3	62.6	2.9	329	11	68	2	1188 0	300	316	9	675	21
144 - 58	Rim	5.51	0.55	967	22	4690 00	1200 0	1.66	0.77	31.8	1.7	3.4	0.7	4.1	0.3	0.5	0.1	87.3	3.0	304	9	57	1	1019 0	310	321	10	348	10
144 - 68	Rim	2.75	0.51	2513	77	4671 00	6300	6.50	1.70	27.2	4.3	14.9	4.4	7.2	1.4	0.3	0.1	183.5	9.4	832	39	153	7	1367 0	360	875	54	2460	100
144 - 72	Rim (i)	6.68	1.00	936	30	4780 00	1400 0	2.80	1.50	32.7	4.5	4.9	2.0	4.4	0.6	0.3	0.0	85.0	3.8	301	12	57	2	1072 0	360	269	12	352	20
144 - 78	Rim	7.29	0.50	674	21	4440 00	1100 0	0.01	0.01	23.3	0.9	1.1	0.1	2.8	0.2	0.2	0.0	62.8	2.9	219	8	42	1	9450	220	167	6	185	7
144 - 80	Rim	10.52	0.68	728	16	4431 00	8900	5.33	0.78	38.8	2.2	12.2	1.1	5.2	0.4	0.6	0.1	67.3	2.0	225	5	44	1	9380	180	176	5	181	6

Spot #	Obs Core/ Rim	Ті	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
144 - 3	Core	48.59	13.00	621	16	4210 00	1600 0	48.00	16.00	131.0	35.0	72.0	21.0	21.2	6.6	1.8	0.6	60.6	4.5	188	6	39	1	9330	420	178	7	221	8
144 - 27	Core	108.1 1	60.00	2240	110	4507 00	8800	12.30	3.20	145.0	27.0	47.0	11.0	19.0	3.3	0.5	0.1	208.0	15.0	612	24	112	3	1003 0	250	1255	59	1354	40
144 - 37	Core	51.26	4.00	1601	41	4600 00	6800	34.50	5.70	95.0	14.0	58.0	11.0	15.4	2.9	1.4	0.3	132.6	6.8	463	19	90	3	1122 0	250	2700	1100	1530	230
144 - 75	Rim	30.37	7.60	406	7	4947 00	9700	3.74	0.89	28.8	2.9	18.8	2.2	5.8	0.7	5.0	0.8	31.4	1.2	142	6	28	1	1128 0	420	89	3	175	7
144 - 7	Core	25.87	5.40	306	32	4080 00	1300 0	38.50	8.30	149.0	44.0	98.0	43.0	24.1	9.0	6.6	2.9	32.8	4.0	101	8	21	2	1031 0	570	60	2	167	16
144 - 20	Rim	13.60	2.70	706	16	4249 00	8900	26.80	1.90	87.0	4.6	51.1	2.7	15.7	1.1	5.2	0.3	64.5	1.6	221	5	43	1	9580	180	176	3	221	5
144 - 28	Rim	7.28	0.63	880	57	4570 00	1200 0	49.00	16.00	62.0	12.0	38.0	11.0	11.8	2.4	2.7	0.7	74.5	6.3	270	20	50	3	1002 0	240	189	18	357	27
144 - 29	Core	3.52	0.85	1000	180	3070 00	1300 0	19.90	4.60	43.7	7.9	17.4	3.6	10.9	1.6	1.0	0.2	97.0	16.0	322	38	68	6	4970	170	179	37	227	15
144 - 44	Core	7.80	0.86	489	25	4170 00	1600 0	16.70	1.90	96.0	9.8	61.6	7.2	14.7	1.6	5.8	0.6	45.9	2.5	155	8	33	1	9310	270	85	5	145	9
144 - 48	Core	8.14	1.10	657	29	5310 00	1700 0	14.00	1.00	54.8	1.5	30.0	1.5	9.8	0.6	2.4	0.2	55.5	2.3	206	12	40	2	1132 0	460	108	3	163	6
144 - 49	Rim (i)	9.91	0.73	793	18	4988 00	8200	13.10	1.60	62.2	4.1	35.5	3.0	12.8	1.0	2.5	0.2	67.9	2.3	230	9	44	1	1023 0	290	199	6	240	8
144 - 53	Core	17.86	1.30	1839	41	4800 00	1600 0	7.47	0.30	34.3	0.7	26.3	1.2	16.6	0.8	2.4	0.2	170.7	4.2	450	15	84	2	7830	240	174	4	159	3
144 - 62	Rim (i)	8.31	0.74	701	17	5240 00	1100 0	0.47	0.76	27.3	1.9	1.6	1.2	2.9	0.5	0.2	0.0	60.5	1.0	223	5	42	1	1045 0	320	162	4	188	5

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
160 - 1	Core	11.78	0.89	932	40	4965 00	9700	0.38	0.18	11.1	0.5	3.3	0.5	5.8	0.5	0.7	0.1	85.1	3.5	222	5	44	1	9200	250	79	3	105	2
160 - 2	Core	12.63	2.70	1270	120	4285 00	9800	29.40	7.60	135.0	35.0	134.0	37.0	31.3	7.7	13.8	3.8	108.0	10.0	392	28	72	4	1046 0	270	103	18	528	18
160 - 3	Core	8.87	1.10	835	40	4780 00	1100 0	3.56	0.32	23.8	2.1	33.4	3.8	12.1	1.2	4.2	0.4	67.6	5.9	288	15	55	2	1209 0	520	41	3	322	12
160 - 5	Core	20.89	1.70	1371	28	4700 00	1900 0	2.20	1.00	29.3	4.9	19.5	4.2	16.0	2.1	4.3	0.7	137.3	4.6	338	7	64	1	8420	160	151	3	178	7
160 - 7	Core	6.79	0.99	1594	50	4140 00	1200 0	0.06	0.02	19.7	0.7	7.4	0.6	10.6	0.8	4.1	0.3	153.5	7.7	411	19	82	2	7400	170	157	9	96	6
160 - 11	Core	3.72	0.37	1327	80	4350 00	1200 0	3.33	0.78	38.7	2.3	8.2	1.7	4.8	0.5	0.4	0.0	109.8	6.9	414	23	85	4	1015 0	270	243	19	517	45
160 - 12	Core	7.37	0.73	1643	33	4590 00	1200 0	2.49	0.28	29.4	1.4	11.1	1.2	9.3	0.6	1.2	0.1	132.2	2.5	399	8	79	2	7700	280	219	7	316	7
160 - 14	Core	8.49	0.82	1447	40	4598 00	9300	0.09	0.06	37.7	1.0	3.5	0.4	6.2	0.5	1.5	0.1	117.0	6.2	454	15	90	2	8410	200	281	9	340	10
160 - 21	Core	8.66	0.84	3460	390	4650 00	1700 0	10.50	6.20	59.0	28.0	60.0	45.0	37.0	26.0	7.4	6.2	303.0	58.0	965	43	182	5	1286 0	470	1640	150	3884	93
160 - 24	Core	8.14	1.30	1350	260	4920 00	1800 0	12.50	1.80	28.2	2.7	14.7	2.2	5.7	1.4	0.4	0.1	135.0	29.0	250	70	42	12	1214 0	450	38	6	321	25
160 - 26	Core	23.20	2.60	1443	61	4460 00	1400 0	4.90	1.30	59.5	5.8	36.2	7.7	21.6	3.0	4.9	0.5	131.1	5.6	405	16	83	2	7580	160	214	15	245	7
160 - 28	Core	7.03	0.53	562	22	4450 00	1300 0	0.02	0.01	11.3	0.5	0.9	0.1	2.1	0.2	0.3	0.0	54.4	2.4	180	6	35	1	9570	180	73	2	141	4
160 - 30	Core	12.88	1.30	566	16	4300 00	1000 0	0.05	0.04	13.1	0.5	1.5	0.2	3.1	0.2	0.6	0.1	55.1	3.0	169	5	34	1	8070	180	62	2	79	2
160 - 32	Core	9.40	0.72	523	43	4770 00	1500 0	0.01	0.01	10.8	0.8	0.9	0.1	2.3	0.2	0.1	0.0	48.1	3.6	152	11	29	2	8770	220	67	6	136	9
160 - 34	Core	9.12	0.57	938	20	4337 00	9000	23.40	1.30	135.7	7.7	129.1	8.3	33.7	1.9	14.1	0.8	94.0	2.4	209	6	40	1	8540	190	76	3	118	4

Spot #	Obs Core/ Rim	Ті	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
160 - 36	Core	4.88	0.43	2606	75	4640 00	1600 0	0.93	0.36	24.7	1.9	8.8	1.2	14.0	0.6	1.9	0.5	247.7	5.0	585	18	109	3	8920	250	388	11	566	16
160 - 39	Core	6.11	0.89	1042	38	4340 00	1600 0	6.93	0.46	47.7	2.9	42.4	3.1	10.5	0.6	11.4	1.3	98.6	2.8	269	7	53	2	1031 0	300	43	5	365	13
160 - 44	Core	12.75	1.10	1299	79	4110 00	1100 0	26.50	4.10	34.5	4.8	10.6	1.5	6.3	1.0	1.9	0.3	120.2	6.3	368	15	74	3	7760	250	96	10	250	17
160 - 49	Core	14.82	1.40	2714	81	4070 00	1300 0	36.50	1.50	186.2	4.4	178.3	5.7	62.7	1.7	8.5	0.5	300.0	11.0	600	24	109	4	7660	190	470	15	424	15
160 - 53	Core	23.08	18.00) 1375	49	4770 00	1900 0	24.00	13.00	136.0	52.0	121.0	70.0	51.0	25.0	8.5	5.1	124.6	6.1	436	8	86	2	1107 0	460	420	13	660	33
160 - 56	Core	5.03	0.68	505	8	4300 00	1200 0	0.04	0.01	12.4	0.4	1.0	0.1	2.6	0.2	0.3	0.0	51.5	1.2	151	4	30	1	8620	230	79	1	139	3
160 - 58	Core	7.65	1.60	3211	54	4352 00	8400	7.40	3.10	42.9	9.2	21.5	6.1	13.4	1.6	0.9	0.2	317.0	13.0	756	23	133	3	1101 0	260	1149	62	2276	75
160 - 62	Core	20.29	1.70	1703	34	4670 00	1400 0	13.80	1.50	125.0	4.6	65.6	3.6	29.4	2.5	23.5	1.6	179.1	6.8	479	12	89	3	1039 0	280	385	12	346	9
160 - 64	Core	16.52	1.10	1487	39	4750 00	1100 0	2.82	0.12	20.1	0.8	22.1	1.1	20.0	1.1	2.4	0.2	161.9	8.8	330	13	60	2	8180	170	106	3	125	7
160 - 66	Core	5.66	0.63	4080	150	4570 00	1800 0	0.64	0.62	59.9	3.1	16.9	1.2	27.0	1.1	4.9	0.2	401.0	10.0	959	29	177	5	7880	230	1227	57	897	29
160 - 68	Core	18.22	1.60	1325	55	4350 00	1400 0	24.90	5.10	102.0	14.0	71.0	11.0	27.3	2.2	13.2	0.6	149.3	6.7	329	8	61	2	7450	150	137	6	216	6
160 - 70	Core	18.46	2.70	2116	93	4920 00	1500 0	30.60	6.00	143.0	24.0	112.0	19.0	35.4	4.8	8.4	1.6	226.6	9.6	530	11	96	4	1079 0	390	338	12	523	21
160 - 72	Core	9.07	0.58	552	7	4530 00	1600 0	0.02	0.01	6.8	0.2	1.8	0.2	3.5	0.2	0.6	0.0	59.7	1.2	159	4	31	1	8140	250	59	1	94	2
160 - 78	Core	7.22	0.67	1890	180	4850 00	1200 0	0.42	0.10	10.8	0.6	9.7	0.7	13.0	1.2	1.0	0.1	179.0	18.0	436	36	81	6	1094 0	390	302	41	727	50
160 - 86	Core	5.47	0.58	939	40	5090 00	1200 0	0.36	0.02	23.1	0.4	2.0	0.2	4.3	0.3	0.5	0.1	81.4	2.2	269	8	53	1	9830	260	131	4	187	4

Spot #	Obs Core/ Rim	Ті	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
160 - 90	Core	9.47	1.90	3100	150	4900 00	1900 0	9.10	4.00	68.0	15.0	43.0	14.0	19.3	2.1	4.9	1.5	304.0	18.0	881	57	155	8	1296 0	270	874	59	1700	110
160 - 92	Core	10.26	0.84	1742	41	4680 00	1100 0	5.92	0.89	44.8	5.9	43.5	7.0	30.3	3.7	10.1	1.7	172.3	4.3	349	9	64	2	8010	160	165	5	256	7
160 - 4	Rim	8.75	3.00	3373	99	5120 00	1300 0	26.20	8.10	117.0	38.0	98.0	46.0	23.8	9.2	12.6	5.4	238.3	6.6	1013	45	186	9	1321 0	250	206	9	845	26
160 - 20	Rim	5.34	1.10	947	31	4113 00	9100	2.00	1.00	21.0	4.3	7.5	3.4	6.3	2.1	1.7	0.9	82.9	3.5	422	23	88	5	1146 0	230	97	2	823	43
160 - 22	Rim (i)	5.04	0.81	873	27	5160 00	1700 0	0.02	0.01	16.2	0.5	1.1	0.2	3.3	0.2	0.3	0.1	77.0	1.6	237	10	46	1	1007 0	410	122	3	218	5
160 - 33	Rim	4.54	0.97	727	16	4570 00	1000 0	0.01	0.01	22.4	0.6	1.1	0.2	2.2	0.2	0.2	0.0	61.7	1.7	220	6	43	1	9850	220	198	6	322	6
160 - 40	Rim (i)	10.80	0.62	1896	51	4970 00	1500 0	7.06	0.56	36.1	2.3	42.8	2.6	12.0	0.9	11.7	0.8	162.3	3.3	519	17	99	3	1105 0	340	121	3	768	23
160 - 47	Rim	2.92	0.52	1742	52	4087 00	8900	0.13	0.06	5.9	0.3	0.8	0.2	3.5	0.4	0.3	0.0	146.1	7.4	516	17	100	3	1047 0	260	150	8	502	17
160 - 57	Rim	13.00	1.80	838	26	4280 00	1500 0	6.75	0.83	47.6	3.5	34.8	3.9	17.5	2.2	4.6	0.4	81.9	3.7	266	10	57	2	1091 0	310	188	8	529	23
160 - 59	Rim	2.96	0.46	1168	35	4168 00	8600	0.17	0.05	12.9	0.4	1.5	0.2	4.4	0.4	0.2	0.0	108.6	2.7	324	8	61	1	1006 0	210	355	8	711	19
160 - 63	Rim	21.99	1.70	579	13	4460 00	1000 0	3.56	0.30	36.9	2.2	20.9	1.8	9.7	1.2	7.3	0.5	53.1	1.7	168	7	37	1	8060	220	45	1	54	3
160 - 65	Rim	9.60	1.30	749	21	4483 00	6500	6.40	1.30	21.2	2.2	5.8	1.2	3.3	0.5	1.6	0.3	60.5	2.1	265	5	56	1	1018 0	300	80	2	240	4
160 - 77	Rim	11.30	1.40	634	29	4640 00	1500 0	0.35	0.18	13.4	1.3	3.7	1.1	4.7	1.0	0.5	0.1	61.3	3.0	169	7	34	1	8250	230	90	4	137	5
160 - 79	Rim	4.80	0.84	3100	110	4360 00	1100 0	3.71	0.73	27.8	2.3	10.1	1.9	7.7	0.8	1.0	0.1	249.5	6.8	968	27	182	6	1022 0	200	259	5	867	30
160 - 81	Rim	9.13	0.72	347	11	4557 00	7200	10.60	2.70	53.0	11.0	56.0	11.0	18.5	3.5	4.0	0.9	36.6	2.0	130	5	28	1	1186 0	290	114	3	426	9

Spot #	Obs Core/ Rim	Ti	2σ	Y	2σ	Zr	2σ	La	2σ	Ce	2σ	Nd	2σ	Sm	2σ	Eu	2σ	Dy	2σ	Yb	2σ	Lu	2σ	Hf	2σ	Th	2σ	U	2σ
160 - 83	Rim	17.13	3.60	676	46	4412 00	7100	11.00	1.80	62.9	8.0	51.3	9.1	20.1	4.1	7.8	1.6	68.0	7.6	213	10	43	1	9720	250	144	7	301	7
160 - 87	Rim	2.78	0.39	1885	90	4534 00	8700	4.53	0.33	23.5	1.3	5.5	0.6	3.4	0.5	0.7	0.1	132.1	6.6	576	23	111	4	1117 0	220	226	20	755	33
160 - 93	Rim	7.41	1.20	1956	50	4970 00	1200 0	18.30	5.20	82.0	19.0	31.4	7.8	13.1	2.1	6.8	2.9	165.7	3.3	525	19	100	3	9920	240	329	11	814	29
160 - 23	Rim (o)	1.72	0.35	3339	58	4630 00	9500	1.57	0.68	19.2	2.6	4.3	1.7	5.2	0.4	0.8	0.2	262.4	9.3	1124	31	206	5	1451 0	300	628	25	1957	43
160 - 37	Rim (i)	43.73	3.40	1048	63	5015 00	9100	11.33	0.75	81.8	4.0	82.4	5.8	48.9	3.6	7.8	0.7	124.0	7.9	215	10	40	1	9450	240	240	14	237	11
160 - 48	Core	7.91	0.54	814	79	4470 00	1500 0	0.03	0.01	10.1	0.6	3.8	0.6	6.1	0.7	2.5	0.4	83.7	8.6	232	15	47	3	7220	180	54	7	37	3
160 - 10	Rim	27.82	6.80	912	39	4760 00	1600 0	8.78	0.62	38.2	2.4	26.5	4.4	10.5	2.2	1.9	0.3	73.6	3.5	368	19	77	3	1485 0	540	161	12	836	37
160 - 16	Core	25.63	9.50	1904	48	3910 00	1600 0	10.10	1.90	56.9	5.0	32.0	19.0	15.8	0.8	3.2	0.4	173.9	7.7	433	15	82	4	6380	300	392	22	270	15
160 - 43	Rim	193.1 4	80.00	715	30	4180 00	1100 0	14.80	2.20	98.3	8.5	52.3	7.6	19.1	2.9	3.5	0.6	71.7	3.2	212	9	42	1	9360	290	223	7	278	7
160 - 50	Rim	510.1 7	66.00	553	98	4760 00	1200 0	30.70	8.90	114.0	27.0	107.0	28.0	37.0	9.9	9.3	2.2	75.0	16.0	140	11	30	2	1059 0	290	220	30	462	37
160 - 54	Rim (i)	437.2 9	100.0 0	607	45	4600 00	1500 0	5.65	0.81	31.7	4.7	24.0	5.9	12.0	3.2	2.6	0.5	59.4	5.8	184	10	40	2	8770	240	75	17	107	24
160 - 82	Core	57.09	12.00	704	49	4439 00	9100	11.20	2.20	58.7	7.1	63.8	5.9	29.7	2.4	8.8	1.2	78.7	6.6	152	9	30	1	7620	140	72	5	68	3

Supplementary material II - Zircon U-Pb dating

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
83 - 1	Core	antecryst	6.070	0.130	0.362	0.010	0.123	0.002	0.79	0.50	1986	18	1989	49	1991	35	100
83 - 3	Core	antecryst	6.100	0.150	0.361	0.009	0.122	0.003	0.68	0.07	1989	22	1985	43	1995	38	100
83 - 11	Core	antecryst	5.650	0.140	0.338	0.009	0.122	0.003	0.56	0.10	1922	21	1878	41	1977	47	98
83 - 14	Core	antecryst	4.270	0.120	0.253	0.008	0.122	0.002	0.88	0.00	1684	23	1454	42	1984	34	86
83 - 16	Core	antecryst	5.280	0.180	0.316	0.015	0.120	0.003	0.59	0.67	1864	29	1771	75	1950	46	95
83 - 21	Core	antecryst	5.540	0.120	0.330	0.011	0.123	0.003	0.68	0.37	1907	19	1835	55	1996	46	96
83 - 29	Core	antecryst	5.460	0.190	0.323	0.011	0.122	0.003	0.81	0.16	1892	31	1805	56	1992	43	95
83 - 37	Core	antecryst	4.650	0.140	0.268	0.007	0.126	0.003	0.79	0.30	1765	27	1531	34	2036	45	87
83 - 50	Core	antecryst	5.780	0.240	0.347	0.017	0.122	0.004	0.79	0.31	1951	40	1918	82	1979	58	98
83 - 62	Core	antecryst	5.858	0.099	0.343	0.008	0.122	0.002	0.48	0.39	1954	15	1900	40	2005	32	97
83 - 7	Rim (i2)	antecryst	6.140	0.170	0.362	0.012	0.122	0.004	0.54	0.37	1995	24	1992	56	1976	53	100
83 - 13	Rim	antecryst	4.110	0.150	0.242	0.008	0.123	0.003	0.72	0.15	1654	30	1396	41	1997	46	84
83 - 17	Rim	antecryst	4.304	0.091	0.253	0.006	0.122	0.003	0.66	0.29	1693	18	1455	33	1987	35	86
83 - 30	Rim	antecryst	5.240	0.120	0.313	0.011	0.120	0.004	0.57	0.69	1858	20	1753	53	1953	54	94
83 - 44	Rim	antecryst	4.890	0.300	0.288	0.019	0.122	0.003	0.96	0.16	1786	53	1641	97	1987	37	92
83 - 46	Rim (i)	antecryst	5.540	0.170	0.332	0.019	0.122	0.003	0.75	0.41	1907	26	1846	90	1976	47	97
83 - 5	Core	xenocryst	2.003	0.069	0.111	0.005	0.130	0.003	0.94	0.62	1115	23	675	28	2101	37	61
83 - 8	Core	xenocryst	5.840	0.200	0.335	0.012	0.126	0.003	0.79	0.15	1952	29	1864	56	2054	47	95
83 - 9	Core	xenocryst	2.670	0.160	0.150	0.007	0.129	0.003	0.96	0.46	1312	42	901	41	2075	41	69
83 - 12	Core	xenocryst	1.420	0.100	0.078	0.006	0.134	0.004	0.92	0.52	894	43	482	38	2141	58	54
83 - 23	Core	xenocryst	3.110	0.300	0.183	0.017	0.123	0.003	0.98	0.17	1416	78	1079	93	1992	40	76

LA-ICP-MS U-Pb measurements for sample USP14-83 (aplitic syenite)

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
83 - 25	Core	xenocryst	2.620	0.130	0.146	0.010	0.133	0.004	0.92	0.62	1324	38	878	54	2136	48	66
83 - 27	Core	xenocryst	4.230	0.360	0.238	0.019	0.128	0.003	0.98	0.42	1663	69	1371	98	2069	39	82
83 - 39	Core	xenocryst	4.910	0.110	0.276	0.007	0.130	0.002	0.86	0.12	1803	18	1571	35	2092	28	87
83 - 43	Core	xenocryst	5.140	0.130	0.305	0.009	0.122	0.002	0.85	0.17	1842	21	1714	42	1988	34	93
83 - 48	Core	xenocryst	4.540	0.160	0.270	0.009	0.121	0.004	0.79	0.11	1737	29	1539	45	1969	53	89
83 - 52	Core	xenocryst	4.090	0.130	0.239	0.009	0.122	0.002	0.93	0.31	1649	26	1382	47	1977	30	84
83 - 56	Core	xenocryst	3.410	0.270	0.203	0.019	0.123	0.003	0.99	0.68	1495	65	1182	100	2000	37	79
83 - 58	Core	xenocryst	4.860	0.120	0.289	0.008	0.120	0.003	0.70	0.15	1794	21	1634	39	1958	38	91
83 - 54	Core	xenocryst	4.560	0.250	0.265	0.015	0.123	0.002	0.96	0.31	1738	46	1514	75	2002	31	87
83 - 63	Core	xenocryst	3.402	0.096	0.200	0.007	0.123	0.002	0.88	0.35	1503	22	1173	37	1998	34	78

LA-ICP-MS U-Pb measurements for sample USP14-83 (aplitic syenite)

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
91 - 10	Rim	autocryst	6.112	0.083	0.361	0.008	0.123	0.002	0.54	0.46	1991	12	1986	38	1995	31	100
91 - 14	Rim (i)	autocryst	6.130	0.110	0.362	0.009	0.123	0.003	0.55	0.34	1993	15	1990	40	1993	40	100
91 - 21	Rim	autocryst	5.940	0.310	0.355	0.015	0.123	0.004	0.85	0.10	1964	46	1960	72	1993	54	100
91 - 26	Rim (o)	autocryst	6.050	0.170	0.353	0.008	0.124	0.003	0.68	0.00	1982	24	1947	40	2007	36	98
91 - 35	Rim	autocryst	5.880	0.100	0.348	0.008	0.122	0.002	0.52	0.41	1960	15	1924	40	1980	34	98
91 - 37	Rim	autocryst	6.080	0.100	0.361	0.008	0.123	0.003	0.49	0.29	1987	14	1984	38	1993	36	100
91 - 46	Rim	autocryst	6.110	0.077	0.360	0.008	0.123	0.002	0.70	0.41	1991	11	1981	37	1995	29	99
91 - 64	Rim	autocryst	5.824	0.077	0.348	0.011	0.122	0.003	0.40	0.48	1950	12	1924	50	1986	44	99
91 - 28	Rim	autocryst	6.030	0.140	0.359	0.010	0.122	0.003	0.46	0.39	1978	20	1977	45	1989	40	100
91 - 24	Core	autocryst	5.880	0.100	0.349	0.011	0.122	0.002	0.73	0.48	1958	15	1928	55	1994	38	98
91 - 43	Core	autocryst	6.170	0.130	0.365	0.008	0.123	0.003	0.37	0.35	1998	18	2006	39	1997	43	100
91 - 47	Core	autocryst	6.100	0.190	0.356	0.009	0.124	0.004	0.06	0.53	1988	27	1962	44	2007	56	99
91 - 49	Core	autocryst	6.190	0.130	0.363	0.011	0.123	0.002	0.88	0.36	2001	18	1995	53	1996	28	100
91 - 54	Core	autocryst	6.090	0.180	0.365	0.013	0.123	0.003	0.77	0.39	1987	26	2003	63	1996	38	101
91 - 63	Core	autocryst	6.120	0.150	0.364	0.009	0.122	0.002	0.76	0.11	1999	20	1999	43	1982	33	100
91 - 65	Core	autocryst	6.160	0.130	0.362	0.009	0.124	0.003	0.70	0.25	1997	19	1992	44	2013	34	100

LA-ICP-MS U-Pb measurements for sample USP14-91 (syenite)

					\		- 1				207Pb		206Pb		207Pb		
Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	/235U date (Ma)	2σ	/238U date (Ma)	2σ	/206Pb date (Ma)	2σ	Conc. (%)
136 - 1	Core	autocryst	5.870	0.230	0.358	0.012	0.120	0.003	0.84	0.21	1956	34	1972	58	1955	50	101
136 - 6	Core	autocryst	5.890	0.110	0.353	0.010	0.121	0.003	0.68	0.35	1963	17	1947	45	1967	42	99
136 - 11	Core	autocryst	5.920	0.130	0.351	0.009	0.124	0.003	0.64	0.23	1969	18	1939	45	2010	39	98
136 - 24	Core	autocryst	5.840	0.110	0.349	0.010	0.122	0.003	0.60	0.38	1952	17	1928	49	1983	37	99
136 - 26	Core	autocryst	6.050	0.190	0.360	0.010	0.122	0.003	0.61	0.10	1982	27	1984	46	1992	49	100
136 - 46	Core	autocryst	6.020	0.160	0.358	0.011	0.122	0.002	0.81	0.22	1981	23	1974	51	1982	32	100
136 - 12	Rim	autocryst	6.130	0.100	0.360	0.009	0.123	0.002	0.70	0.50	1994	14	1983	44	1994	31	99
136 - 16	Rim (i)	autocryst	5.910	0.130	0.353	0.009	0.123	0.003	0.43	0.55	1962	19	1948	41	2000	38	99
136 - 17	Rim (o)	autocryst	6.050	0.150	0.358	0.010	0.122	0.002	0.78	0.10	1987	20	1972	45	1990	34	99
136 - 29	Rim	autocryst	6.090	0.110	0.362	0.009	0.121	0.003	0.56	0.48	1988	16	1992	43	1981	39	100
136 - 39	Rim (o)	autocryst	5.954	0.097	0.359	0.009	0.121	0.003	0.57	0.46	1968	14	1985	42	1965	41	101
136 - 51	Rim (i)	autocryst	6.030	0.130	0.359	0.008	0.121	0.003	0.45	0.31	1979	19	1978	40	1980	38	100
136 - 52	Rim (o)	autocryst	5.960	0.120	0.359	0.010	0.121	0.003	0.63	0.60	1970	18	1976	47	1969	40	100
136 - 55	Rim (o)	autocryst	5.896	0.098	0.353	0.009	0.120	0.002	0.67	0.38	1960	15	1948	44	1961	37	99
136 - 57	Rim	autocryst	6.000	0.150	0.360	0.010	0.121	0.004	0.42	0.51	1975	22	1982	50	1970	64	100
136 - 62	Rim	autocryst	5.970	0.120	0.357	0.010	0.120	0.003	0.75	0.21	1971	18	1969	47	1965	38	100
136 - 64	Rim	autocryst	6.060	0.120	0.360	0.012	0.123	0.003	0.83	0.63	1984	18	1981	56	1996	39	100
136 - 4	Core	antecryst	3.650	0.230	0.219	0.013	0.119	0.002	0.97	0.07	1552	49	1272	67	1943	35	82
136 - 8	Core	antecryst	4.981	0.095	0.316	0.008	0.115	0.002	0.72	0.28	1815	16	1770	39	1874	33	98
136 - 28	Core	antecryst	4.720	0.150	0.284	0.008	0.123	0.004	0.50	0.14	1777	29	1609	39	2001	57	91
136 - 34	Core (i)	antecryst	5.170	0.140	0.310	0.008	0.121	0.003	0.42	0.30	1847	23	1740	41	1968	52	94
136 - 50	Core	antecryst	4.350	0.160	0.257	0.012	0.125	0.003	0.84	0.21	1700	31	1473	59	2021	46	87

LA-ICP-MS U-Pb measurements for sample USP14-136 (monzonite)

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
136 - 61	Core	antecryst	4.050	0.130	0.254	0.009	0.116	0.002	0.86	0.16	1644	26	1460	47	1894	37	89
136 - 9	Rim	antecryst	4.390	0.200	0.276	0.011	0.118	0.002	0.92	0.27	1713	39	1569	55	1929	36	92
136 - 19	Rim	antecryst	4.674	0.096	0.297	0.009	0.115	0.003	0.55	0.61	1761	17	1675	45	1879	44	95
136 - 47	Rim	xenocryst	3.402	0.073	0.212	0.006	0.116	0.002	0.87	0.28	1504	17	1245	33	1889	31	83
136 - 37	Core	xenocryst	5.890	0.150	0.341	0.010	0.129	0.003	0.80	0.35	1958	22	1893	49	2082	38	97
136 - 18	Core	xenocryst	5.760	0.150	0.330	0.010	0.126	0.002	0.89	0.07	1945	24	1835	46	2049	30	94
136 - 32	Core	xenocryst	5.580	0.130	0.321	0.009	0.127	0.002	0.81	0.03	1912	20	1792	43	2059	33	94
136 - 35	Core (o)	xenocryst	5.520	0.140	0.321	0.008	0.127	0.003	0.66	0.04	1903	22	1793	39	2048	40	94
136 - 63	Core	xenocryst	6.060	0.130	0.361	0.008	0.123	0.003	0.40	0.34	1984	19	1985	39	2002	47	100
136 - 65	Core	xenocryst	5.590	0.170	0.320	0.010	0.126	0.003	0.85	0.08	1912	26	1790	51	2036	40	94

LA-ICP-MS U-Pb measurements for sample USP14-136 (monzonite)

Spot #	Obs Core/	Obs	207Pb	2σ	206Pb	2σ	207Pb	<u>2</u> σ	Rho	Rho	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Conc.
	Rim		/2350		/2380		/206PD		/5/08	80/70	(Ma)		(Ma)		(Ma)		(%)
144 - 5	Core	autocryst	5.830	0.180	0.352	0.009	0.121	0.004	0.39	0.30	1963	26	1942	45	1965	59	99
144 - 16	Core	autocryst	6.230	0.100	0.367	0.008	0.123	0.002	0.65	0.29	2007	14	2017	39	1995	31	100
144 - 18	Core	autocryst	5.790	0.170	0.340	0.013	0.123	0.003	0.85	0.15	1944	26	1887	62	1999	37	97
144 - 19	Core	autocryst	4.552	0.083	0.290	0.009	0.115	0.003	0.56	0.48	1740	15	1642	43	1871	41	94
144 - 21	Core	autocryst	5.820	0.140	0.349	0.012	0.123	0.003	0.69	0.52	1960	20	1929	58	1990	44	98
144 - 26	Core	autocryst	6.000	0.170	0.355	0.011	0.122	0.003	0.86	0.02	1974	25	1959	52	1989	46	99
144 - 35	Core	autocryst	6.030	0.110	0.358	0.009	0.122	0.002	0.65	0.16	1980	16	1974	41	1987	35	100
144 - 42	Core	autocryst	5.990	0.100	0.357	0.009	0.122	0.002	0.81	0.48	1976	15	1966	42	1984	29	99
144 - 55	Core	autocryst	2.070	0.120	0.164	0.007	0.091	0.002	0.93	0.42	1133	38	979	37	1444	46	86
144 - 57	Core	autocryst	6.224	0.092	0.373	0.008	0.123	0.003	0.53	0.40	2007	13	2043	40	1991	36	102
144 - 64	Core	autocryst	2.540	0.160	0.191	0.011	0.096	0.002	0.96	0.48	1290	44	1126	57	1561	40	87
144 - 67	Core	autocryst	5.650	0.130	0.333	0.008	0.122	0.003	0.66	0.01	1922	19	1852	40	1976	38	96
144 - 69	Core	autocryst	4.030	0.260	0.263	0.014	0.111	0.004	0.92	0.39	1635	52	1502	70	1819	57	92
144 - 71	Core	autocryst	5.190	0.160	0.316	0.009	0.120	0.002	0.82	0.10	1850	26	1769	45	1959	35	96
144 - 4	Rim	autocryst	5.960	0.140	0.351	0.008	0.123	0.002	0.80	0.24	1967	20	1937	38	1999	34	98
144 - 10	Rim	autocryst	6.290	0.170	0.368	0.010	0.123	0.003	0.71	0.10	2015	24	2017	46	1999	49	100
144 - 22	Rim	autocryst	6.170	0.120	0.364	0.008	0.122	0.002	0.66	0.25	1999	16	2002	39	1985	34	100
144 - 24	Rim	autocryst	6.090	0.110	0.362	0.008	0.122	0.002	0.59	0.28	1990	16	1990	40	1991	33	100
144 - 34	Rim	autocryst	6.040	0.130	0.356	0.009	0.122	0.003	0.59	0.30	1980	18	1963	43	1984	38	99
144 - 38	Rim (i)	autocryst	6.050	0.130	0.361	0.009	0.123	0.002	0.75	0.51	1983	19	1987	44	1997	35	100
144 - 41	Rim	autocryst	5.878	0.092	0.348	0.008	0.122	0.002	0.76	0.25	1960	13	1927	40	1993	28	98
144 - 47	Rim	autocryst	6.140	0.150	0.359	0.008	0.124	0.003	0.80	0.31	1995	22	1978	40	2010	44	99

LA-ICP-MS U-Pb measurements for sample USP14-144 (granodioritic porphyry)

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
144 - 52	Rim	autocryst	6.140	0.110	0.363	0.008	0.122	0.003	0.53	0.38	1994	16	1996	40	1987	36	100
144 - 54	Rim	autocryst	6.075	0.099	0.361	0.008	0.121	0.002	0.55	0.30	1986	14	1986	38	1976	33	100
144 - 58	Rim	autocryst	6.047	0.074	0.364	0.008	0.122	0.002	0.63	0.35	1982	11	2001	36	1977	30	101
144 - 72	Rim (i)	autocryst	5.830	0.120	0.352	0.010	0.121	0.002	0.86	0.74	1950	18	1942	48	1968	34	100
144 - 78	Rim	autocryst	5.940	0.110	0.357	0.008	0.122	0.003	0.46	0.29	1969	15	1965	37	1986	38	100
144 - 80	Rim	autocryst	6.190	0.110	0.365	0.009	0.122	0.002	0.64	0.22	2002	16	2007	41	1989	33	100
144 - 1	Core	xenocryst	6.430	0.170	0.372	0.010	0.126	0.003	0.74	0.01	2035	23	2037	47	2046	39	100
144 - 3	Core	xenocryst	6.130	0.130	0.366	0.009	0.122	0.004	0.42	0.67	1993	19	2008	44	1986	55	101
144 - 9	Core	xenocryst	2.310	0.180	0.171	0.012	0.097	0.002	0.99	0.41	1204	52	1017	63	1560	36	84
144 - 27	Core	xenocryst	5.910	0.110	0.366	0.009	0.118	0.002	0.91	0.30	1962	16	2011	44	1928	27	102
144 - 33	Core	xenocryst	6.100	0.130	0.366	0.010	0.121	0.003	0.54	0.47	1990	18	2017	44	1971	48	101
144 - 37	Core	xenocryst	5.450	0.250	0.354	0.015	0.112	0.004	0.81	0.17	1884	40	1952	72	1817	60	104
144 - 45	Rim	xenocryst	6.040	0.230	0.358	0.014	0.123	0.003	0.81	0.28	1981	33	1971	67	1999	46	99
144 - 74	Core	xenocryst	5.420	0.360	0.365	0.024	0.107	0.002	0.97	0.03	1911	57	2030	110	1755	38	106
144 - 75	Rim	xenocryst	6.250	0.150	0.364	0.009	0.124	0.004	0.38	0.44	2011	21	2003	41	2012	52	100

LA-ICP-MS U-Pb measurements for sample USP14-144 (granodioritic porphyry)

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
160 - 1	Core	autocryst	6.310	0.140	0.369	0.010	0.124	0.003	0.31	0.33	2019	19	2026	45	2023	49	100
160 - 2	Core	autocryst	6.320	0.160	0.369	0.012	0.125	0.003	0.78	0.21	2020	22	2023	57	2027	39	100
160 - 3	Core	autocryst	6.470	0.150	0.376	0.010	0.125	0.003	0.55	0.32	2041	21	2056	47	2020	39	101
160 - 7	Core	autocryst	6.260	0.170	0.370	0.012	0.125	0.004	0.48	0.45	2011	24	2027	54	2024	58	101
160 - 11	Core	autocryst	6.320	0.110	0.363	0.009	0.125	0.002	0.68	0.33	2020	15	1995	43	2023	34	99
160 - 12	Core	autocryst	6.510	0.120	0.376	0.009	0.126	0.003	0.76	0.40	2047	16	2057	44	2046	39	100
160 - 14	Core	autocryst	6.320	0.140	0.372	0.010	0.124	0.003	0.55	0.42	2020	20	2037	46	2020	49	101
160 - 30	Core	autocryst	6.330	0.150	0.368	0.009	0.124	0.003	0.20	0.37	2021	21	2020	40	2007	47	100
160 - 32	Core	autocryst	6.409	0.097	0.369	0.009	0.126	0.002	0.59	0.29	2033	13	2024	41	2039	33	100
160 - 36	Core	autocryst	6.518	0.094	0.370	0.008	0.127	0.002	0.60	0.32	2048	13	2027	39	2057	30	99
160 - 39	Core	autocryst	6.450	0.110	0.367	0.009	0.128	0.002	0.42	0.50	2038	15	2015	44	2068	32	99
160 - 44	Core	autocryst	6.190	0.150	0.368	0.012	0.124	0.003	0.64	0.47	2002	21	2017	57	2013	35	101
160 - 49	Core	autocryst	6.400	0.170	0.370	0.012	0.125	0.002	0.82	0.16	2031	23	2030	55	2025	34	100
160 - 64	Core	autocryst	6.510	0.140	0.372	0.009	0.128	0.003	0.66	0.26	2047	19	2037	44	2065	36	100
160 - 66	Core	autocryst	6.304	0.096	0.367	0.009	0.125	0.002	0.58	0.46	2020	14	2013	40	2031	33	100
160 - 78	Core	autocryst	6.610	0.150	0.382	0.010	0.126	0.002	0.89	0.23	2060	20	2086	44	2047	27	101
160 - 86	Core	autocryst	6.490	0.140	0.374	0.011	0.127	0.003	0.68	0.41	2044	19	2048	51	2058	36	100
160 - 4	Rim	autocryst	6.370	0.150	0.366	0.011	0.124	0.002	0.74	0.18	2028	20	2009	51	2012	34	99
160 - 20	Rim	autocryst	6.200	0.180	0.364	0.010	0.124	0.003	0.88	0.03	2003	26	2002	45	2017	35	100
160 - 22	Rim (i)	autocryst	6.300	0.140	0.366	0.010	0.125	0.003	0.55	0.46	2017	20	2011	47	2021	38	100
160 - 29	Rim	autocryst	6.220	0.100	0.366	0.009	0.124	0.003	0.61	0.43	2006	15	2010	45	2005	36	100
160 - 33	Rim	autocryst	6.360	0.170	0.373	0.009	0.125	0.004	0.48	0.11	2026	24	2042	40	2019	54	101

LA-ICP-MS U-Pb measurements for sample USP14-160 (granodiorite)

Spot #	Obs Core/ Rim	Obs	207Pb /235U	2σ	206Pb /238U	2σ	207Pb /206Pb	2σ	Rho 75/68	Rho 86/76	207Pb /235U date (Ma)	2σ	206Pb /238U date (Ma)	2σ	207Pb /206Pb date (Ma)	2σ	Conc. (%)
160 - 40	Rim (i)	autocryst	6.390	0.150	0.362	0.010	0.128	0.002	0.78	0.22	2034	20	1989	47	2078	35	98
160 - 41	Rim (o)	autocryst	6.160	0.130	0.360	0.011	0.123	0.003	0.74	0.36	1998	19	1983	51	2001	38	99
160 - 47	Rim	autocryst	6.200	0.160	0.364	0.010	0.124	0.002	0.81	0.03	2003	23	1999	47	2015	35	100
160 - 59	Rim	autocryst	6.150	0.120	0.363	0.010	0.124	0.002	0.80	0.34	2001	16	1997	48	2022	32	100
160 - 63	Rim	autocryst	6.380	0.450	0.379	0.023	0.124	0.004	0.89	0.04	2040	57	2070	110	2004	62	101
160 - 79	Rim	autocryst	6.350	0.120	0.371	0.008	0.124	0.002	0.75	0.04	2024	16	2036	38	2016	33	101
160 - 81	Rim	autocryst	6.294	0.086	0.369	0.008	0.124	0.002	0.61	0.37	2017	12	2023	38	2017	33	100
160 - 83	Rim	autocryst	6.210	0.110	0.368	0.011	0.123	0.003	0.52	0.62	2005	15	2021	50	1992	43	101
160 - 87	Rim	autocryst	6.530	0.170	0.380	0.009	0.124	0.003	0.77	0.08	2049	23	2074	42	2014	37	101
160 - 24	Core	xenocryst	6.700	0.190	0.382	0.014	0.128	0.004	0.62	0.59	2072	25	2087	65	2070	59	101
160 - 46	Core	xenocryst	6.730	0.160	0.379	0.011	0.130	0.003	0.51	0.35	2081	22	2073	49	2094	46	100
160 - 64	Core	xenocryst	6.510	0.140	0.372	0.009	0.128	0.003	0.66	0.26	2047	19	2037	44	2065	36	100
160 - 78	Core	xenocryst	6.610	0.150	0.382	0.010	0.126	0.002	0.89	0.23	2060	20	2086	44	2047	27	101
160 - 86	Core	xenocryst	6.490	0.140	0.374	0.011	0.127	0.003	0.68	0.41	2044	19	2048	51	2058	36	100
160 - 92	Core	xenocryst	6.500	0.130	0.381	0.010	0.126	0.003	0.58	0.45	2045	17	2081	45	2034	37	102

LA-ICP-MS U-Pb measurements for sample USP14-160 (granodiorite)

Supplementary material III – Lithos Publication (2020)

"Orosirian magmatism in the Tapajós Mineral Province (Amazonian Craton): the missing link to understand the onset of Paleoproterozoic tectonics"

Orosirian magmatism in the Tapajós Mineral Province (Amazonian Craton): the missing link

to understand the onset of Paleoproterozoic tectonics

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1. Introduction

The age of the onset of modern-style plate-tectonics remains a matter of controversy. Some authors claim that a subduction-like tectonic regime, not a perfect analogue to present-day tectonics but somehow similar, operated as early as the Archean (e.g. Calvert and Ludden, 1999; Laurent et al., 2014a; Santosh et al., 2013). A peculiar characteristic of Archean tectonics would be its intermittence, since a stable, long-lived subduction wouldn't be possible in a significantly hotter mantle (O'Neill et al., 2007; Van Hunen and Moyen, 2012). On the other hand, based on the age of the oldest ophiolites, blueschists and UHP terranes, Stern (2005) postulated that the onset of modern-style tectonics was as late as the Neoproterozoic. Accordingly, only by that time Earth's lithosphere would be sufficiently cold and dense to sink into subduction zones and generate the expected P-T paths and, ultimately, obduction.

Several lines of evidence have been followed to discuss Earth's tectonic evolution. Firstly, one may consider one time slice –the Archaean— and discuss the tectonic regimes operating then. Different models have been proposed and good summaries can be found in Bédard (2018). They range from non-

actualistic (thus suggesting a late onset of modern plate tectonics) to actualistic or near actualistic (thus more consistent with an early onset). A second line investigates the evolution of observable (preserved) features through time. Condie (2018) listed relevant geologic and geochemical changes during Earth's evolution such as the increasing proportion of basalts with "arc-like" signature and zircon age peaks, the latter suggesting an increase in the production of continental crust. However, the author is less emphatic with respect to tectonic-regime transition. Amongst these observations, the continental crust general characteristics are especially relevant. Whereas Archean crust is essentially dominated by tonalite-trondhjemite-granodiorites (TTG) suites (e.g. Condie and O'Neill, 2010; Kearey et al., 2009; Moyen and Martin, 2012), the petrogenesis of which still debatable (Martin et al., 2014), modern continental crust is on average andesitic, LILE-enriched, follows the calc-alkaline differentiation trend and is most commonly formed by hydrated-mantle melting in subduction-zones (Condie and O'Neill, 2010; Hawkesworth and Kemp, 2006).

Regardless of the style and the onset of modern-tectonics, less emphasis has been put on the Proterozoic. Bédard (2018) understands it as an eon of changing tectonic styles from stagnant-lid and overturn-upwelling-zones in the mantle (vertical tectonics), to a modern-style slab-pull driven tectonic regime. This debate frames the discussion on the geology of the South American Platform (Almeida et al., 2000). In this region, the Paleoproterozoic Era is the most significant in terms of continental crust addition, with two main events recognized: one at the 2.3 - 2.1 Ga interval (Rhyacian); and another at 2.1 - 1.8 Ga (Orosirian) (Giustina et al., 2009), both well represented at the Amazonian Craton (AC) (Fig. 1a). The Orosirian event in particular predominates at southern AC, on an area known as Tapajós Mineral Province (TMP) (Fig. 1b). Accordingly, this part of the AC is characterized by the occurrence of different and compositionally heterogeneous granitic suites of calc-alkaline to shoshonitic affinity with subordinate volcanic manifestations and anorthosite – mangerite – charnockite – granite (AMCG) rock associations (Santos et al., 2000; Tassinari and Macambira, 1999; Valério et al., 2018).

The economic relevance of the TMP has been well known ever since the 1960's, when many artisanal miners began to exploit alluvial gold (until late 90's, official numbers point to a production of more than

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200 tons of gold (Faraco et al., 1997)). Most recent papers highlight the potential of the province for magmatic-hydrothermal deposits (Fig. 1b shows a few examples), not only for precious metals but also for base metals such as copper, molybdenum and tin, the majority directly or indirectly related to the Orosirian igneous sequence (Bettencourt et al., 2016; Biondi et al., 2018; Borges et al., 2009; Borgo et al., 2017; Cassini, 2016; Juliani et al., 2005, 2002; Santos et al., 2001). The well-preserved 1.86 Ga quartz-alunite epithermal system described by Juliani et al. (2005) clearly demonstrates the potential for shallow-level mineral-systems in the TMP, and highlights the economic importance of Precambrian cratonic areas throughout the world.

Deposits such as porphyry Au-Cu ±Mo and epithermal (high-sulfidation) are usually associated with hydrous and oxidized (i.e. amphibole and magnetite bearing), arc-related, intermediate to acid intrusions that upon decompression will exsolve fluids and volatiles that are responsible for mobilizing, transporting, disseminating and/or precipitating the metals in veins and veinlets (Cooke et al., 2013; Pirajno, 2009; Richards, 2011; Sillitoe, 2010). It is crucial however, that the magmas presents the correct fO_2 (which for porphyry systems varies between the Δ FMQ +2 and HM oxygen buffers (Sun et al., 2015)) so sulfur predominates as SO_4^{2-} (more soluble than S^{2-} in silicic melts) and chalcophile metals behave incompatibly during the magmatic evolution, concentrating on the exsolved fluids.

Despite the importance of accessing the petrologic evolution and investigating the sources of the different igneous suites, the TMP still lacks such studies and additional efforts are required. Regarding the petrogenetic constraints of granitic rocks, it's been demonstrated by Clemens et al. (2011) and by Clemens and Stevens (2012) the fundamental role that sources have in controlling the geochemistry variability of the melts generated. Mechanisms such as peritectic phase entrainment and/or co-entrainment of accessory minerals act controlling the budget of compatible elements (e.g. Mg, Hf, Zr, Ti and REE) whereas source composition accounts for the variation in incompatible elements (e.g. Rb, Ba, Sr and K). Furthermore, the formation of igneous bodies is quite complex and despite the source influence, the overall composition of the system might be influenced by differentiation of the primary
mafic magma (in case of mantle derived silicic melts), crustal melting within deep crust hot zones and by melt mixing upon migration and installation on shallower crustal levels (Annen et al., 2015).

With the purpose of establishing magmatic correlations and enlightening the debate on sources and tectonic processes, this study addresses the petrologic evolution of the igneous rocks within the 2.00 – 1.86 Ga interval described at the TMP. The implications of this approach are also relevant in terms of metallogenetic potential at southern AC, since it will ultimately demonstrate the igneous suites that are compatible with a hydrous and oxidized petrologic trend. Additionally, a better characterization of these rocks represents an important step towards establishing a holistic and regional metallogenetic model. Hence, the results and discussion presented at this paper may be considered as important contributions for a better understanding of the tectonic evolution of the AC, and more globally of the Proterozoic Earth.

2. Geological Setting

2.1. Regional context and crustal architecture

The Amazonian Craton (AC) is a tectonically stable area since the end of the Grenvillian orogeny (ca. 1.2 Ga ago) of approximately 4.6 x10⁶ km², composed of Paleoproterozoic tectonic blocks juxtaposed against ancient Archean nuclei and surrounded by Meso- and Neoproterozoic mobile belts (Santos et al., 2000; Tassinari and Macambira, 1999). The AC has been traditionally divided into tectonic/geochronologic provinces on the basis of U-Pb and Sm-Nd isotope geochemistry. Two main subdivision schemes are commonly used: Tassinari and Macambira (1999); and Santos et al. (2000). Both models divide the AC in roughly N—S trending blocks and consider the Tapajós region (shaded rectangle in Fig. 1a) as the result of a Paleoproterozoic collisional orogen, that was built in arc-related igneous rocks of calc-alkaline affinity that predominates at the south-central AC. In Tassinari and Macambira's (1999) model, the craton's assembly involved juxtaposition of Archean tectonic blocks between 2.20 and 1.95 Ga. In this case, the Tapajós region represents a series of juvenile magmatic-arcs formed on a continent-ocean subduction-controlled regime that ultimately resulted in collision between

the craton's nuclei and a tectonic block to the southwest. On Santos' et al. (2000) model (Fig. 1a), the Archean is restricted to the Carajás Province and the the Tapajós Mineral Province (TMP) is located on the limit between the Tapajós-Parima and Central Amazon provinces, at the south-central part of the AC (Figures 1a and 1b). The authors understand the Tapajós region as new crust accreted to the AC through a series of magmatic and island arcs.

Alternative concepts and models have been proposed with acquisition of new and more precise isotopic and geophysics data. For example, Fernandes et al. (2011), in view of the progressively younger ages of the igneous units towards NE, proposed that at ca. 1.88 Ga the central part of the AC was affected by a flat-subduction period that was responsible for the arc-related units migration towards the Central Amazon block. Juliani et al. (2015) and Carneiro et al. (2019) claim that the arc-related sequence at the TMP was built on Archean basement. E-W well marked lineaments are intrinsically related with the ancient basement of the craton and would extend to the TMP all the way from the 500 km apart Carajás Province. Considering its orogenic to post-orogenic tectonic setting, a peculiar feature of the TMP is the lack of fold-and-thrust-belts and/or HPLT metamorphic terrains. Such particularity led Juliani et al. (2015) to suggest that the tectonic regime at the Tapajós region varied from weakly extensional to slightly compressive, similar to the pre-compressive stage of the Andean Orogeny in central Chile during the Jurassic (Ramos, 2010). Intra- and back-arc rift basins filled with pyroclastic and epiclastic rocks from the magmatic-arc are evidence of the extensional characteristic of the Tapajós tectonics, previously recognized only at the post-orogenic stage (Juliani and Fernandes, 2010; Santos et al., 2004, 2002, 2001; Vasquez et al., 2002). Interestingly, the convergence rate, direction, sediment supply, topography and age of the subducting plate are features that can influence the tectonic regime at the magmatic arc, and according to Juliani et al. (2015) could also explain the strong subcrustal-tectonic-erosion (Von Huene and Lallemand, 1990; Wagreich, 1993) responsible for the destruction of significant part of the geologic record related to the convergence at the TMP.

2.2. Lithostratigraphy

The lithostratigraphic units in the TMP comprise: i) the Jacareacanga Group (>2.0 Ga) represented by a metamorphosed volcano-sedimentary sequence and metabasic rocks; ii) the granitoids of the Cuiú-Cuiú Complex (ca. 2.04 - 1.99 Ga), that with the Jacareacanga Group form the region's basement; iii) the Jamanxim (ca. 2.00 - 1.98 Ga), Creporizão (ca. 1.98 - 1.95 Ga), Tropas (ca. 1.90 - 1.88 Ga), Parauari (ca. 1.89 - 1.87 Ga) and Maloquinha intrusive suites (ca. 1.87 - 1.86 Ga); and (iv) the volcanic rocks of the Iriri Group (1.89 - 1.87 Ga) (ages after Santos et al., 2004, 2001, 2000). The igneous rocks with ages between 2.00 and 1.95 Ga will be addressed as the older magmatic sequence, whereas the suites younger than 1.90 Ga will be treated as the younger magmatic sequence. The Cuiú-Cuiú Complex consists mainly of tonalites, diorites and granodiorites, whereas the Jamanxim, Creporizão, Tropas, Parauari and Maloquinha suites are essentially granitic. Most of the extrusive rocks described at the TMP belong to the Iriri Group, however, a few older examples were described by Lamarão et al. (2002) (the ca. 2.00 Ga rhyolites from the Vila Riozinho Formation at eastern TMP) and by Tokashiki (2015), ca. 1.97 Ga undifferentiated rhyolites at southwest TMP. Table 1 presents a summary of the main lithostratigraphic units identified at the TMP, with their respective description and tectonic setting.

3. Methods

Sample preparation for whole-rock chemical analysis was performed at the Laboratory of Sample Preparation of the Geosciences Institute of University of São Paulo and involved: i) hand sample disaggregation with a hydraulic press; ii) sample crushing and pulverization with tungsten swing mill; and iii) quartering of the pulps. The analytical procedure followed the standard protocol by ACME Laboratories in Vancouver (Canada). Rock pulps were mixed with lithium tetraborate, molten, casted into homogeneous glass disks and latter analyzed through X-ray fluorescence spectroscopy (XRF). The same fused glass disks were used for trace elements analyses through ICP-MS, and reproducibility of the results, guaranteed by multiple analyses of reference materials, duplicates and blanks, is better than 1% for major-oxides and better than 5% for trace elements. Additional information on analytical procedures

is available at www.acmelab.com. Whole-rock geochemistry results were handled with GCDKit (Janoušek et al., 2006) and later used for the geochemical modelling routines.

Geochemical modelling was carried out using GCDKit and further R programming Janoušek et al. (2016). We used simple mass balance (for major elements), and Rayleigh-type fractionation using published partition coefficients (for trace elements), following the method outlined in Janoušek et al. (2016). This allows to investigate whether a suite of samples may represent liquids related by fractional crystallization of a cumulate made of minerals of known compositions, but in unknown proportions. When possible, we used real mineral compositions acquired in the relevant suites of the TMP (Echeverri Misas 2010) for the major elements calculations. Amphiboles from the TMP classify predominantly as ferro-hornblende with rarer magnesio-hornblende, pyroxenes as pigeonite and biotites as annite. For plagioclase and K-feldspar, the compositions were estimated through petrography and Fe and Ti oxides were considered as pure phases. The partition coefficients used for calculation of trace elements were taken from GERM database (http://earthref.org) and from Rollinson (1993).The quality of a given model can be assessed using the sum of squared residuals (R²),that measures the differences between the calculated and actual differentiated melts for each element. R² values closer to 0 correspond to models with a better numerical fit.

U-Pb geochronology was performed with the Sensitive-High-Resolution-Ionic-Microprobe (SHRIMP-IIe/MC) of the High Resolution Geochronology Laboratory of the University of São Paulo, Brazil (GeoLab). For zircon separation, samples were initially crushed, then sieved and the fraction between 0.150 – 0.060 mm was concentrated using a Frantz magnetic separator and, afterwards, treated with heavy liquids (bromoform, d =2.89 g/cm³). The zircon grains were handpicked and mounted on doublesided adhesive plate with the TEMORA 2 standard. Imaging with both back-scattered electrons (BSE) and cathode-luminescence (CL) to expose respectively surface imperfections and internal structure complexities of the grains were acquired using a Quanta 250 FEI, with XMAX CL detector at the GeoLab. The SHRIMP-IIe primary beam of O_2^- ions is set for the analytical procedure with a current of 3 nA and spot size of 30 μ m. The secondary beam analytical conditions involves a source slit of 80 μ m and mass

resolutions for ¹⁹⁶(Zr₂O), ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³⁸U, ²⁴⁸(ThO) and ²⁵⁴(UO) between 5.000 and 5.500 (1%), with residues <0.025. Data acquisition involved six mass range scans for each selected grain, with 12 to 15 grains analyzed per sample and a reference value (Temora 2) every 4 zircon grains. The ²⁰⁴Pb correction followed the proposal after Stacey and Kramers (1975), after which data was reduced and evaluated with SQUID-1.06 and concordia diagram were plotted with ISOPLOT3 (Ludwig, 2003). Further detailed analytical conditions and procedures might be found at Eddy et al. (2018).

Whole-rock Sm-Nd isotopic analyses were carried out at the Geochronology Laboratory from University of Brasilia, Brazil, by thermal ionization mass spectrometry (TIMS), and followed the protocol described at Gioia and Pimentel (2000). Rock pulps were initially mixed with ¹⁴⁹Sm - ¹⁵⁰Nd spike solution and dissolved in Savillex capsules. Sm and Nd extraction followed conventional cation exchange techniques through Teflon columns containing LN-Spec resin (HDEHP – diethylhexil phosphoric acid supported on PTFE powder). Once extracted, Sm and Nd samples were loaded on Re filament of double filament assembly. Isotopic measurements were performed on a Finnigan MAT-262 mass spectrometer using one fixed central electron multiplier and 7 adjustable Faraday cups accomplished in static mode. The ¹⁴³Nd/¹⁴⁴Nd ratio was normalized using ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219, and the decay constant used was of 6.54 x10⁻¹² /y. Reproducibility of the results was evaluated with blanks and analyses of the rock standard BCR-1 (uncertainties for Sm/Nd and ¹⁴³Nd/¹⁴⁴Nd are better than 0.5% and 0.005% respectively), that yielded a ¹⁴³Nd/¹⁴⁴Nd ratio of 0.512632 ±2 (1 σ , n=5), Nd concentration of 28.73 ppm and Sm concentration of 6.66 ppm, attesting the accuracy of the method.

4. Field Relationships and Petrography

4.1 The Older Magmatic Sequence (ca. 1.99 – 1.95 Ga)

The older magmatic sequence (OMS) on the studied area comprises the Creporizão Intrusive Suite (CRP) and undifferentiated rhyolites. The CRP (Figs. 2a to 2d) is composed by granodiorites, monzonites, syenites, monzo- and syenogranites, the two latter are rather common on the TMP and were frequently identified on the drill-cores. Granites are typically leucocratic, porphyritic, magnetite-bearing and

composed of K-feldspar, quartz, plagioclase, biotite and amphibole (Figs. 2a and 2b), with ubiquitous microgranular mafic enclaves (Fig. 2c) and aplite dykes. Titanite, allanite and zircon were recognized as accessory phases. Plagioclase phenocrysts vary from euhedral to anhedral and are commonly affected by saussuritic alteration, especially where the anorthite contents are higher (between An₅₅ and An₆₈). K-feldspar constitutes subhedral and anhedral crystals. Biotite is the most common mafic mineral, with zircon and allanite as common inclusions. Amphibole, titanite and opaque minerals occur associated with biotite as agglomerates (Fig. 2b). Figure 2a illustrates a rapakivi texture, where a microcline megacryst is rimmed by saussuritic plagioclase. Secondary textures such as the substitution of primary igneous plagioclase by secondary K-feldspar were described on these lithotypes and are mainly a consequence of hydrothermal alteration.

CRP syenites and monzonites are texturally similar but syenites have more K-feldspar (an example of syenite is presented at Fig. 2d). Both rocks are characterized by the presence of plagioclase and K-feldspar phenocrysts, euhedral and subhedral, the former commonly saussuritized. Quartz is scarce and defines anhedral crystals on the matrix. Mafic minerals are rare and represented by anhedral biotite and opaques. These rocks are commonly identified at the TMP and the contacts with the granites are transitional (Fig. 2e₁) and sometimes not clear.

Granodiorites (Fig. 2f) are rarer and the contact with the granites is predominantly abrupt as demonstrated on Figure 2e₂ (less frequent transitional contact was also described). They are usually leucocratic, porphyritic and similar to the granites in terms of mineralogical composition, varying essentially on the magnetite and amphibole contents (more abundant on the latter). Plagioclase phenocrysts are commonly euhedral, saussuritic and show compositions from An₅₅ (labradorite) to rarer An₇₁ (bytownite). Quartz and K-feldspar, both subhedral and anhedral, are the main phases in the matrix. Amphibole and biotite, euhedral and subhedral respectively, form aggregates that occupy the interstices amongst feldspar phenocrysts.

The older volcanic rocks identified at the TMP by Tokashiki (2015) are described as rhyolites and are divided into two facies. Facies A (Fig. 3a₁) defines topographic domes in the field, is commonly flow-

banded and dark-colored. It is composed of K-feldspar and plagioclase, subhedral and anhedral quartz crystals, with amphibole as the main mafic. Epidote and chlorite, when present, are related to the alteration of amphibole. Facies B (Fig. 3a₂) is compositionally similar, but defines dykes intruded on the granitoids of the Cuiú-Cuiú Complex (basement). It is typically red-colored, porphyritic, dominated by spherulites, with euhedral plagioclase phenocryst and biotite as the main mafic mineral. Despite their synchronicity with CRP, the older rhyolites so far haven't been attributed or correlated with other lithostratigraphic units from the TMP.

4.2 The Younger Magmatic Sequence (ca. 1.89 – 1.86 Ga)

The younger magmatic sequence (YMS) includes the Parauari and Maloquinha Intrusive Suites (PAR and MLQ respectively) and the Iriri Group. Echeverri Misas (2015) reported a cross-cutting relation between the OMS and YMS, yet, these relations are rarely seen on the field.

PAR is petrographically similar to CRP, comprising monzonites, monzo- and syenogranites and syenites (Fig. 3b) with rather common mafic enclaves. Granites are porphyritic, grey colored, with plagioclase, K-feldspar and quartz megacrysts distributed on a biotite- and hornblende-rich matrix, with titanite, apatite, zircon, allanite and magnetite as accessories. Plagioclase and K-feldspar are subhedral to euhedral and define phenocrysts, the former varies from albite to An₂₀ (oligoclase). Biotite and amphibole are anhedral and together with euhedral titanite and magnetite define mafic agglomerates on the matrix. Monzonites and syenites are quite similar to the granites, but in contrast, lack amphibole and quartz megacrysts.

The Iriri Group comprises andesites, dacites and rhyolites with both effusive and explosive examples (Figs. 3c₁ and 3c₂). Andesites define dykes that are commonly found on granitoids of the OMS (Fig. 3d), are aphanitic (with minor occurrences of porphyritic andesites) and dark colored. They are mostly made of euhedral and subhedral plagioclase and mafic minerals (amphibole, biotite, titanite, zoisite and opaques). Titanite and amphibole are euhedral or subhedral, the latter often replaced by biotite, and are associated with opaque minerals (pyrite in most cases). Dacites and rhyolites are predominantly

aphanitic, brown to reddish colored, commonly massive with a few examples presenting flow-banding. The matrix is shperulitic with common sericite-filled fissures.

On regional scale, MLQ defines ovoid bodies of a few kilometers across. Amongst all igneous suites of the TMP, MLQ is the one that shows the narrowest compositional range. The unit is composed by syenogranite frequently displaying microgranular felsic enclaves. The rocks are leucocratic, porphyritic (Fig. 3e) and red-colored, dominated by euhedral to anhedral perthitic K-feldspar and quartz megacrysts, plagioclase phenocrysts and biotite as the main mafic, with titanite, zircon and opaque as accessories. Plagioclase is typically low-Ca, with predominance of An₂₅ (oligoclase).

5. Geochemistry

5.1. Major Elements and Classification Diagrams

Janoušek et al. (in press) have shown that a handful of key indicators define the chemistry of granitoids, and are most useful in identifying various types: acidity, alkalinity, aluminosity, ferroan or magnesian nature and sodic or potassic nature. The first two are neatly expressed in the R1-R2 diagram of De la Roche et al. (1980), whereas additional projections are required to fully explore the other properties.

On the R1-R2 diagram, monzo- and syenogranites from the OMS plot on the granite and alkali-granite fields, monzonites and syenites plot predominantly on the quartz-monzonite, quartz-syenite and syenite fields, and granodiorites fall on the granite, granodiorite and tonalite fields (Fig. 4a). The coeval volcanic units are geochemically homogeneous and classify as rhyolites and alkali-rhyolite (Fig. 4c). The SiO₂ contents for both plutonic and volcanic rocks vary between 57.6 and 78.3 wt.%, with syenites displaying the lowest concentrations (a summary of whole-rock geochemistry results is presented at Table 2). Besides their lower silica contents, other discernible features of syenites are their higher K₂O and FeO_t concentrations (up to 7.9 and 5.4 wt.% respectively). Following the classification proposed by Peccerillo and Taylor (1976) (Fig. 4e), granites belong to the high-K calc-alkaline or to the shoshonite series, whereas syenites and rhyolites are essentially shoshonitic.

The R1-R2 plot for the YMS shows that the PAR granites scatter through the granite, granodiorite and tonalite fields, and syenites and monzonites plot respectively on the quartz-monzonite and quartz-syenite fields (Fig. 4b). These rocks fall on the transition between the high-K calc-alkaline and shoshonitic magmatic series (Fig. 4f). MLQ is comparatively more restrict, plots on the granite and alkali-granite fields and is essentially shoshonitic. When contrasted with PAR, this unit shows a distinct geochemistry signature, with higher K₂O and lower MgO and FeOt contents. From the igneous units studied, the Iriri Group is the one that covers the widest compositional range (55.3 \leq SiO₂ \leq 79). It varies from rhyolites and alkali-rhyolites to less abundant andesites, lati-andesites, dacites, quartz-latites and quartz-trachytes. These rocks either belong to the high-K calk-alkaline or to the shoshonitic magmatic series (Figs. 4d and 4f).

Aluminosiy is one of the important features in granitoid chemistry, and can be discussed using several projections. In the ternary diagram after Moyen et al. (2017) (Figs. 5a and 5b), the trend defined by the OMS rocks is roughly horizontal to positive sloped, around the A/CNK=1 line (inset on Fig. 5a). For the YMS two contrasting behaviors may be identified (inset on Fig. 5b). On one hand, most of the Iriri volcanics and the PAR intrusives plot in the bottom half of the diagram, along a trend with a positive slope. One the other hand, some Iriri samples as well as the MLQ intrusive plot along a negatively slopped array in the peraluminous side of the diagram. Both groups overlap near the AI + (Na+K) apex (the granite minimum).

The B—A diagram after Villaseca et al. (1998) (Fig. 5c) depicts the same property in a slightly different way. The OMS defines a clear negatively-sloped trend, where the more primitive units plot on the metaluminous field whereas the most evolved units spread towards the low- and felsic-peraluminous fields (I-P and f-P respectively). The YMS samples define two contrasting trends on the diagram. The PAR granitoids define a weakly negative slope, with the samples distributed between the metaluminous and I-P fields, similar to the CRP. In contrast, the MLQ samples are more strongly peraluminous and vary from highly-peraluminous to low- and f-P, with rare metaluminous examples.

5.2. Trace Elements

Figures 6a and 6b show chondrite-normalized REE plots for the TMP igneous units and, in general terms, the OMS REE patterns are more strongly fractionated than the YMS (non-normalized La/Yb vs Yb plot from Fig. 7a also demonstrates this pattern). Within the OMS, CRP granites s.I (comprising syeno-, monzogranites and granodiorites) and rhyolites show equivalent levels of REE fractionation that vary from moderate to high (average (La/Yb)_N for these units is of 19.8, Tab. 2). Within CRP granites, two different trends are discernible (both are shown on Fig. 6a). A less fractionated one with small negative Eu anomaly and another one, more strongly fractionated and negligible or null Eu anomaly. The petrologic implications of these different trends will be further discusses on section 7.1.1. The REE distribution is more homogeneous for CRP syenites, and fractionation falls within a much narrower interval ($5.4 \le (La/Yb)_N \le 24.3$), with an average of 14.8. Despite the occurrence of a few positive Eu_N/Eu^{*} values, the Eu anomalies are weakly to moderately negative for the OMS and all units show average ratio of 0.6 (Tab. 2). Regarding the Dy/Yb vs MgO plot, the OMS tends to spread on the vertical axis and the ratio varies between 1.0 and 2.4 (Fig. 7b).

For the YMS, Figure 6b reveals that PAR and Iriri show equivalent patterns on the REE spidergrams whereas MLQ presents a subtle different behavior. The former two tend to spread on the diagram from Figure 7a around moderate La/Yb ratios (with values between 8.3 and 27.9 for PAR and from 7.1 and 27.4 for Iriri (Tab. 2)). In addition, PAR shows mildly negative to positive Eu anomalies whereas Iriri is characterized by lower Eu_N/Eu^* . MLQ, in contrast, shows a less fractionated REE pattern, with 4.5 \leq (La/Yb)_N \leq 15.6 and is accompanied by the most expressive Eu anomalies (all samples have Eu_N/Eu^* ratio bellow 0.65 as expressed on Tab. 2).

Regarding multi element patterns, the spidergram for the OMS shows a predominantly homogeneous behavior for most elements (average CRP granites and syenites overlap on Fig. 6c). Minor differences might be identified mostly for compatible elements (Zr, Sm, Dy, Y, Yb and Lu). The Sr/Y vs Y plot (Fig. 7c) shows that the OMS units vary from low (2.0) to high values (close to 50.0) and the average Ga/Al*10⁴ ratios fall between 1.9 to 2.2.

Multi element spidergram for YMS reveals significant differences among the units, in particular between PAR and MLQ, with the Iriri volcanic rocks mostly displaying an intermediate behavior. In addition to Eu as already mentioned, MLQ shows clear depletions in Ba, Sr, P and Ti, and is enriched in Th, U and Pb. Iriri mimics this exact geochemical pattern, yet less intensely (except for Sr, to which enrichment is also observed). PAR, on the other hand, lacks Ba and Eu depletions and shows only a minor decrease in Sr, P and Ti. The Sr/Y plot (Fig. 7c) shows that PAR and Iriri scatter between low and high ratios that vary from 2 and 80. MLQ decouples from this behavior and shows essentially lower ratios (Sr/Y \leq 5). Additionally, MLQ shows the highest Ga/Al*10⁴ ratios (Tab. 2) among the TMP units, with values between 2.2 and 4.6 (averages for PAR and Iriri are respectively 2.4 and 2.1).

6. Radiogenic Isotopes

6.1. U-Pb Geochronology

Four granitoid samples were collected for geochronology from the central TMP, at locations shown in Fig. 1. In general terms, the zircon grains from all samples can be classified into two textural categories: category 1 zircon, which were preferentially considered for the analyses, consists on euhedral to subhedral crystals, with well preserved oscillatory growth zoning and more rarely xenocrystic cores; category 2 is defined by subhedral to anhedral, dark crystals on the cathodoluminescence (CL) images (Fig. 8) and common metamict cores. Both types present apatite as the most common inclusion and the elongation ratio is between 3:1 and 2:1.

Sample USP14-160 show smaller grains (average elongation of 2:1) and is characterized by the lowest U contents (average of 144 ppm) and by a greater proportion of inherited cores. Magmatic zircons are concordant to weakly discordant, with a discordia with upper intercept at 1994.3 ±8.8 Ma (Fig. 8a), interpreted as the crystallization age. Sample USP14-179 shows more elongated zircon grains (3:1 aspect ratio) with the highest U contents (average of 287 ppm) that are represented by darker colors on the CL image and predominantly euhedral morphology (type 1 zircon). 8 discordant and 7 concordant grains define a discordia with upper intercept at 1958.9 ±5.1 Ma (Fig. 8b) interpreted as the magmatic

age. Samples USP14-136 and USP14-36 show a greater proportion of type 2 zircon grains, with frequent metamictic cores. These portions of the grains were avoided during the analyses in view of the possible radiogenic Pb loss. For USP14-136, 5 concordant and 7 discordant grains resulted in a discordia with upper intercept at 1970.4 ±7.7 Ma (Fig. 8c), interpreted as its magmatic age. USP14-36 shows predominantly concordant grains that define a concordia age of 1954.9 ±4.2 Ma (Fig. 8d). Table 3 shows the summarized isotopic results for the U-Pb and Sm-Nd pairs acquired at this study. The precise U and Th contents, additional isotopic ratios and the respective errors are available as Supplementary Data.

All the results presented at this study are in agreement with ages presented by other authors for the OMS, including the Cuiú-Cuiú Complex, Jamanxim and the Creporizão Intrusive Suites that show ages between 2.0 and 1.95 Ga (e.g. Santos et al., 2004, 2001, 2000).

6.2. Whole-rock Sm-Nd

This study presents a compilation of 27 whole-rock Sm-Nd isotope analyses which are summarized at Table 3. ϵ Nd_(t) for each sample was calculated preferentially at their respective U-Pb crystallization age and, if not available, we used the pluton's crystallization age (results are presented on Figure 9). Within OMS, the ¹⁴³Nd/¹⁴⁴Nd ratio varies between 0.511112 and 0.511424 and the ϵ Nd_(t) from -8.36 and +1.69. Syenites show the highest ϵ Nd_(t), whereas the values acquired for granites and rhyolites are more negative and fall around -2.0, with an isolated value at -8.36. T_{DM} model ages concentrate between 2.4 and 2.3 Ga for the rhyolites and granites, and around 2.1 Ga for the syenites, with an older age at 2.95 Ga.

For the younger igneous sequence, the ¹⁴³Nd/¹⁴⁴Nd ratio falls between 0.511030 and 0.511679 and is accompanied by ϵ Nd_(t) that varies from -5.85 to -0.18. Among these units, the PAR Suite is the one that shows the lowest ¹⁴³Nd/¹⁴⁴Nd ratios (from 0.511030 to 0.511048). Accordingly, the ϵ Nd_(1.88) values are slightly more negative than the ones acquired for CRP (-5.85 $\leq \epsilon$ Nd_(1.88) \leq -4.77), and yields T_{DM} model ages around 2.5 Ga. The isotopic signature of the slightly younger extrusive rocks from the Iriri Group is significantly different, with ϵ Nd_(1.87) closer to 0. Samples NP-316 and NP-303B stand as the only exceptions, the latter in fact shows a strong affinity with the isotopic signature presented by PAR. The MLQ Suite resembles the isotopic signature presented by the Iriri Group and is characterized by mildly negative $\epsilon Nd_{(1.86)}$, with values that vary from -2.64 to -0.28. T_{DM} model ages for both units vary from 2.5 and 2.1 Ga.

7. Discussion

7.1. Magmatic Evolution and Fractionation Trends

In general, the older magmatic sequence (OMS) is characterized by similar ¹⁴³Nd/¹⁴⁴Nd ratios (as demonstrated on Fig. 9 and Tab. 3), which is coherent with a closed system evolution and allows the modelling of fractionation trends. The younger magmatic sequence (YMS) however, in particular Iriri and MLQ, show more significant variations regarding Nd isotopes and likely evolved with external contributions.

7.1.1. Fractionation within the Older Magmatic Sequence

Amongst all lithotypes within the OMS, granodiorites show the highest MgO, FeO_t and TiO₂ contents, and might be considered as potential parental magmas for a differentiation sequence. These rocks define two different REE patterns as demonstrated on section 5.2. One of these trends is less fractionated, presents higher contents of middle- and HREE and a small negative Eu anomaly, whereas the other is more strongly fractionated and don't show Eu anomaly (both granodiorites are identified on Fig. 6a and on the diagrams from Fig. 7). The trace element ratios presented at Figure 7 are relevant tools in this context since it allows discriminating the evolution of these rocks, in particular the involvement or not of amphibole due to its preference in partitioning preferentially middle-REE over HREE. This is in contrast with pyroxene, for which fractionation between middle- and HREE is less intense (i.e. $Kd_{Am}^{Dy} / Kd_{Am}^{Yb} > Kd_{Px}^{Dy} / Kd_{Px}^{Yb}$,Kd's from GERM database (http://earthref.org) and Rollinson (1993)). Accordingly, one of the granodiorites is characterized by higher Dy/Yb, La/Yb and Sr/Y ratios (approximately 2.0, 40 and 30 respectively), whereas the other has much lower values (1.5, 12 and 5 respectively) and is apparently part of the general trend defined by the other units. This set of geochemistry characteristics suggests the existence of two contrasting petrologic trends within the OMS, one dominated by amphibole fractionation, and one by pyroxene fractionation. Figure 10 presents Harker diagrams for selected major oxides and trace elements, with the modelling arrays and the respective minerals involved.

The parental magma for the clinopyroxene dominated series is the older (1994 Ma) granodiorite sample. The evolution is compatible with fractionation of a diorite cumulate (cumulate compositions follow the R1-R2 classification after De la Roche et al. (1980)) made of plagioclase (68%), biotite (16%), magnetite (7%), clinopyroxene (6%) and titanite (3%), and generates a monzogranite liquid for a degree of crystallization (F_c) of 0.37. The R² of 0.592 points to a good correlation between real and theoretical evolved liquids (C_L), which is also demonstrated by the blue array on the diagrams of Figure 10.

For the amphibole dominated series, our model starts from a granodioritic liquid that evolved to alkaligranite compositions. Such petrologic is consistent with fractionation of 43 – 57 % of a plagioclasedominated cumulate (up to 55%), with amphibole (30%), K-feldspar (10%), titanite (3%) and magnetite (2%), generating a monzonite cumulate. The synchronous rhyolites apparently follow the same petrologic trend. As amphibole is progressively extracted from the magma, the Dy/Yb ratio decreases with differentiation (Fig. 7b) whereas La/Yb increases (Fig. 7a) (Sr/Y is only weakly affected as Y removal is counterbalanced by profound Sr decrease as plagioclase is also involved). Despite the accuracy of the model (indicated by the black array on the diagrams of Fig. 10, with R² =0.083), samples tend to scatter for Rb, V, Sr and K, in contrast to the more homogeneous pattern for Fe, Mg, Ti and Ca oxides, reflecting the heterogeneity of the parental magma regarding incompatible elements budget.

Within the OMS, syenites evolve on a silica-poorer fractionation trend than the amphibole and clinopyroxene bearing series (as represented by the light-red area on the Harker diagrams from Fig. 10). Their petrologic evolution is compatible with the crystallization of K-feldspar as a major phase (up to 64% of mineral proportion on the cumulate), accompanied with plagioclase (20%), biotite (7%), apatite

(4%), clinopyroxene (3%) and ilmenite (2%), for a F_c between 0.33 and 0.37 and a cumulate that could be understood as a K-feldspar rich crystal mush. The R² of 0.622 reveals a good correlation between the calculated and real differentiated liquids. This evolution is controlled only by nominally anhydrous minerals, in contrast with the amphibole bearing one. Additionally, our models show that magnetite is not involved in the petrologic evolution of the syenites, whereas it is present in the evolution modeled for the amphibole and pyroxene bearing series, reflecting higher fO_2 latter two. The petrogenetic relevance of these observations is further discussed in section 7.2.

7.1.2. Fractionation within the Younger Magmatic Sequence

Within the units from the YMS, geochemical modelling for the PAR Suite was not possible due to the lack of samples and the impossibility to define clear trends. Nonetheless, the moderate to high La/Yb and Sr/Y ratios of this unit are consistent with amphibole fractionation and thus with hydrous magmas. Additionally, the lack of Ba, Sr and Eu depletions indicate that PAR evolved through early extraction of plagioclase, also consistent with an hydrous magmatic evolution (Grove et al., 2012; Naney, 1983).

Samples from the Iriri Group scatter on Harker diagrams (Fig. 11), with reasonably well-defined trends for some major oxides (CaO, Fe₂O₃ and MgO). In contrast, the strongest variations are mainly observed for incompatible trace-elements (Rb and Sr) and for K₂O. For the intermediate volcanics the best results were acquired for andesitic initial liquids that evolved to dacitic compositions. This evolution is consistent with fractionation of an amphibole-dominated (up to 43 %) cumulate, with lesser amounts of biotite (27%) and plagioclase (25%), with apatite (4%) and magnetite (1%) as accessories, for a F_c around 0.42 and a gabbroic composition. The R² of 2.146 is mathematically tolerable, however, it reveals only a moderate level of correlation between theoretical and real differentiated liquids. The acid lavas of the Iriri Group, on the other hand, are more homogeneous in major elements, with a few scattered samples for Rb. The modeling shows that an initial dacitic liquid differentiated to rhyolite through the fractionation of plagioclase (55% of the cumulate), K-feldspar (36%), clinopyroxene (8%) and titanite (1%) as accessory, for a F_c within the range 0.41 – 0.46, and a syenitic cumulate. The R² of 0.089 that indicates a good level of correlation and the accuracy of the model, is much lower than the one acquired for the intermediate units model, suggesting a minor degree of weathering for the latter (indeed, intermediate volcanics tend to scatter more for both major oxides and trace elements). Furthermore, there is a clear disconnection between the intermediate and the acid compositions that cannot be modelled as one single trend. Thus, either different sources or continental crust assimilation must have played a role. Nd isotopes support the latter hypothesis.

MLQ shows a smaller compositional range, and a trend compatible with a granitic initial composition that differentiated to syenogranite through fractionation of plagioclase (36%), K-feldspar (36%), clinopyroxene (25%) and ilmenite (3%) for a small degree of crystallization ($F_c = 0.22$) of a monzonitic cumulate. The anhydrous characteristic of the MLQ magmatism translates into Dy/Yb values that tend to cluster between 1.5 and 2.0, and into low Sr/Y and La/Yb ratios (Fig. 7), all inconsistent with amphibole fractionation. Furthermore, the modelling results for MLQ show that fractional crystallization by itself doesn't account for the geochemical variability of the unit: the R² of 1.6, among the highest of the igneous suites modeled, suggests that fractionation cannot explain the whole of MLQ's petrologic evolution.

7.2. Constraints on Petrogenesis and Implications for Paleoproterozoic Tectonics in the AC

A first-order petrogenetic difference modelled in the different magma types of the TMP is the opposition between "wet" and "dry" magmas. "Wet" magmas, including part of the CRP and PAR suites evolve by fractionation of an amphibole-rich cumulate. They correspond to magma types identified as being metaluminous to somewhat peraluminous, middle-REE depleted, that differentiates towards higher La/Yb and Sr/Y and lower Dy/Yb ratios. In contrast, "dry" magmas evolutions are controlled by an amphibole-free cumulate, with clinopyroxene being the dominant mafic phase. These magmas are metaluminous to mildly peraluminous, middle- and HREE depleted and differentiate towards higher La/Yb and Sr/Y with only a subtle decrease in Dy/Yb. Experimental petrology (Grove et al., 2012; Naney,

1983) shows that, in hydrous magmas, the onset of plagioclase crystallization is delayed, resulting in lesser depletions in Sr, Ba or Eu compared to dry magmas during the course of fractionation.

Within the OMS, part of the Creporizão Intrusive Suite (CRP) is one of the "wet" magma types. It occurs as mutually intrusive bodies with diffusive or unclear contact and contains ubiquitous mafic enclaves and rapakivi textures. Its geochemistry characteristics, together with the average $\epsilon Nd_{(1.95)}$ of -2.77 (Tab. 3) connects CRP with wet and oxidized mafic magmas that are most typically generated on subductionzones through melting of the hydrated mantle wedge. In this particular tectonic scenario the newly formed magmas would be either hydrous basalts or high-Mg andesites (e.g. Grove et al., 2012; Pichavant et al., 2002) that rise through the lithosphere and stall at lower to mid-crustal levels. As new batches of mafic magma are accumulated, they create a "hot zone" (Annen et al., 2006) where magmas evolve and interact with the preexisting crust, through a range of processes collectively described as MASH (melting-assimilation-storage-homogenization Hildreth and Moorbath (1988)) and felsic magmas are generated as a result of these processes. Annen et al. (2015) proposed that fractionation of a primary mafic magma may occur in many stages, where a batch of basaltic magma can be injected into a more differentiated andesitic crystal mush in a shallower hot zone. This model adequately explains the generation of different intrusions within the 1.98 - 1.95 Ga interval and the field relations described in the OMS of the TMP. Assimilation of preexisting continental crust by the primary mafic melts is evidenced by the moderately negative $\epsilon Nd_{(1.95)}$ values for the CRP rocks (Tab. 3). The coeval and compositionally equivalent rhyolites described by Tokashiki (2015) in the southwest TMP show similar petrologic evolution (Fig. 10) and $\epsilon Nd_{(1.96)}$ values (average of -1.87) and, consequently, should be understood as the extrusive manifestation of the CRP magmatism. The synchronous CRP syenites, characterized by higher $\epsilon Nd_{(1.95)}$ could represent early differentiated batches of magma provided by the mantle wedge under the same tectonic context, with null or negligible crustal contamination. The "dry" condition of syenites could be explained by corner flow induced mantle melting.

In contrast, the 1.99 Ga granodiorite is geochemically distinctive and cannot be correlated with the CRP. Despite the age proximity, this sample belongs to an alternative petrologic trend (clinopyroxene

bearing) characterized by higher Dy/Yb, La/Yb and Sr/Y ratios. It also displays more evolved $\epsilon Nd_{(1.99)}$ (-8.36) and a greater proportion of inherited zircon cores, consistent with the larger involvement of a crustal component. In view of the tectonic context and the slightly older age, these rocks could represent earlier stages of the magmatic-arc, where the first batches of primary mafic melts were contaminated by subcrustal erosion debris (Fernandes and Juliani, 2019) or by trench derived sediment upon the onset of subduction at ca. 2.0 Ga. Even though strongly negative $\epsilon Nd_{(t)}$ were also reported in granitic rocks by Echeverri Misas (2015) and Sato (1998), such values are scarce in the region, and this can be a consequence of the lesser preservation potential of early-arc igneous rocks, accounting for the predominance of CRP or late-arc magmatism in the preserved magmatic record in the TMP.

Despite their metaluminous to mildly peraluminous character, the PAR rocks (approximately 70 million years younger than CRP), show more strongly negative $\epsilon Nd_{(1.88)}$ values (average of -4.85) compared to the older CRP. This could be the result of crust-contaminated or melting of metasomatized mantle in a mature-arc situation. The essentially metaluminous nature of these rocks, coupled with the absence of diagnostic negative correlation between differentiation and aluminosity (Moyen et al. 2017) rules out crustal melting as an important process in the petrogenesis of the PAR. The PAR displays the characteristic features of hydrous magmas (lack of Ba, Sr and Eu depletions (Fig. 6b and 6d) reflecting the delay of plagioclase fractionation; moderate to high Sr/Y and La/Yb ratios compatible with amphibole fractionation), and a high-K to shoshonitic affinity. All these features resemble the postorogenic magmatism signature defined by Bonin (1990), which is dominated by metasomatized mantle melting. As proposed by this author, a typical orogenic rock association will comprise mainly calcalkaline units that are directly related to hydrated mantle-wedge melting, transitioning to alkaline magmatism through collision-related high-K calc-alkaline suites over, usually, less than 100 Ma.

The first pulses of the Iriri Group volcanics are synchronous with the PAR magmatism (Juliani et al., 2002; Santos et al., 2004, 2001), yet contrasting $\epsilon Nd_{(T)}$ suggests different sources. Similar to the PAR, the Iriri intermediate volcanic rocks are high-K to shoshonitic (Fig. 4f) and show the characteristic features of wet magmas. The acid portion of the Iriri Group, although not directly petrologically related, shows essentially the same $\epsilon Nd_{(1.87)}$ values. In both cases, the $\epsilon Nd_{(1.87)}$ close to 0 suggests metasomatized

subcontinental-lithospheric-mantle (SCLM) as the most plausible source. Fernandes et al. (2011) and Fernandes and Juliani (2019) proposed that from ca. 1.95 until 1.88 Ga the subducting slab under this part of the AC progressively flattened. The first batches of magma generated in this transitional tectonic environment would form by melting of metasomatized mantle wedge, resulting in metaluminous and hydrous mafic melts that upon differentiation generate the PAR suite and the initial bursts of the Iriri volcanism. As steeper angle subduction is resumed, slab-detachment or slab-retreat would result in asthenospheric mantle inflow and melting of the previously metasomatized SCLM would be a consequence of the resulting thermal anomaly. This process explains the high-K to shoshonitic affinity of the Iriri rocks and their more primitive $\epsilon Nd_{(1.87)}$, that becomes progressively more negative as a result of increasing continental crust assimilation as these magmas ascend to shallower hot zones. Various degrees of assimilation are also consistent with the impossibility to model the whole suite as one single fractional crystallization series.

The MLQ Suite is granitic and compositionally homogeneous (Fig. 4b) and varies from metaluminous to highly peraluminous (Fig. 5). But in contrast to CRP and PAR, MLQ doesn't define a negative trend on the A-B diagram and in the projection from biotite diagram, this unit either plots close to the A/CNK =1 line or defines a negative trend. The MLQ source is thus clearly distinct from that of the other units, and in fact shows characteristics more commonly associated with crustal melting (e.g. Clemens et al. (2011); Moyen et al. (2017)). However, the $\varepsilon Nd_{(1.86)}$ values close to 0 (Tab. 3) of MLQ are not consistent with this, but rather with a mantle source. Lastly, the unit's petrological trend is best modelled in terms of dry magmatic evolution. In many respects (except the peraluminous character), the MLQ geochemistry is similar to the Iriri Group (particularly its acid portion). We therefore propose that the MLQ magmas were similar to the Iriri magmas, but differentiated to peraluminous compositions via crustal contamination.-In our proposed scenario, asthenosphere upwelling not only promoted metasomatized SCLM melting but also crustal extension, facilitating magma ascent and promoting crustal melting, thus favoring mantle-crust interactions and crustal assimilation by the rising melts (Fernandes and Juliani, 2019). A very similar model has been proposed for the 1.88 Ga São Gabriel AMCG association (approximately 500 km north of TMP) (Valério et al., 2018). The dry character of MLQ magmas is

compatible with the early-anorogenic alkaline granites defined by Bonin (1990). Higher Ga/Al ratios also point to a probable crustal contribution and reinforces MLQ's early-anorogenic affinity (Patiño Douce, 1997; Whalen et al., 1987). Therefore, Iriri's and MLQ's characteristics are indicators of a transitional tectonic environment, from a post-collisional or post-orogenic to an early-anorogenic tectonic setting, with increasing degrees of crustal contamination of originally SCLM melts.

7.3. Metallogenic Implications

Genetic models proposed for the mineral occurrences of the TMP include orogenic-gold deposits, intrusion-related gold systems (IRGS) and porphyry/epithermal mineral systems (Lopes and Moura, 2019; Juliani et al., 2005; Santos et al., 2001; Tokashiki, 2015) or combination of these (Biondi et al., 2018). The Tocantinzinho gold mine in the central TMP is hosted by 1.97 Ga granitoids that show geochemical, geochronological and hydrothermal alteration features similar to other mineral occurrences of the TMP (e.g. Palito, Batalha and Patrocínio mineralizations) themselves interpreted as magmatic-hydrothermal systems (Cassini, 2016; Echeverri Misas, 2015; Juliani et al., 2002). Regardless of the metallogenetic model it is axiomatic that the formation of a mineral deposit requires the presence of fertile rocks, and magmatic-hydrothermal systems in particular are genetically related with hydrous, oxidized, intermediate to acid intrusions shallowly emplaced (Pirajno, 2009; Richards, 2015, 2011; Sun et al., 2015). Through geochemical modelling it was possible to access the petrologic evolution of the different igneous suites at the TMP within the age range of 1.99 - 1.86 Ga and consequently identify which suites are potentially fertile for the formation of magmatic-hydrothermal mineral systems.

It is thus meaningful that the first pulses of OMS in the TMP at ca. 1.99 Ga present geochemical characteristics diagnostic of an anhydrous evolution. Consequently, this stage of arc evolution may not be considered economically fertile. As the subduction evolves the characteristics of the arc magmatism change and the igneous rocks within the 1.98 - 1.95 Ga interval correspond to hydrous and oxidized

magmas that may be considered as potentially fertile for the formation of porphyry (Cu-Au ±Mo) and epithermal systems.

The OMS is made of multiple batches of rocks emplaced over tens of millions years, with diffuse or transitional contacts. Interactions between magmatic fluids from these intrusions are perfectly plausible and particularly efficient from a metallogenetic perspective. In fact, rather than associated with a single homogeneous pluton, a typical porphyry system is most commonly associated with magma chambers that are constantly refilled by new batches of melt. This has been well illustrated by Large et al. (2018)who proved the importance of a complex magmatic evolution for the formation of the porphyry (Au-Cu) Ok Tedi deposit in Papua New Guinea, where new injections of magma triggered the last stage of the magmatic-hydrothermal system which ultimately lead to the mineralization. Regionally, a similar model has been proposed for the Patrocínio area (Cassini, 2016) on the central TMP, where the gold mineralization is hosted by mutually intrusive CRP granites and syenites and consists of quartz-pyrite gold bearing veins and veinlets, preferentially found in zones of strong potassic alteration. In summary, the CRP Suite, precisely its amphibole dominated series, presents the geochemistry and petrologic features to be considered as potentially fertile for magmatic-hydrothermal mineralizations.

Based on its hydrous nature, the ca. 1.89 Ga PAR Suite is also fertile. In this study we understand PAR as representative of a mature magmatic-arc. This geological context is particularly favorable for the formation of both Cu-Au and Au-only porphyry deposits that involve incorporation of residual gold rich sulfides from the mantle (Richards, 2015). The Batalha (porphyry-Au (Juliani et al., 2002)) and the Palito (porphyry Au-Cu) deposits are good examples of magmatic-hydrothermal systems hosted in PAR metaluminous to peraluminous granitoids. Nevertheless, an additional effect should be considered with respect to the YMS economic potential, since these igneous suites could also act remobilizing the previously formed mineralization, at the CRP magmatism for example. Mineralized Iriri dykes intruding CRP granites (Fig. 3d) may represent example of this process. Although this style of mineralization has not been described in details yet, we suggest that it represents a promising prospective target in the TMP.

8. Summary and Concluding Remarks

The results presented on this study show strong geochemical and petrologic evidence for a subductioncontrolled tectonic regime regulating the petrogenesis on the south-central Amazonian Craton at the 1.99 – 1.89 Ga interval (Figure 13 shows schematic tectonic sketches illustrating the ideas presented at this study). Accordingly, the tectonic and petrologic evolution of the Tapajós Mineral Province and its lithostratigraphic units might be briefly summarized as it follows:

- The first stage of the older magmatic sequence (OMS), at ca. 2.0 Ga (Fig. 13a), was responsible for the generation of anhydrous magmas (with clinopyroxene as a fractionating phase) with a strong crustal component (and consequently negative εNd_(1.99) values) due to subcrustal-erosion or trench derived sediment contamination during the onset of subduction. This early crustal component disappears as the arc matures.
- After this initial phase, arc-magmatism between 1.98 and 1.95 Ga involves the formation
 of metaluminous to mildly peraluminous, hydrous and oxidized (magnetite and
 amphibole-bearing) intrusive suites, with coeval volcanic manifestations. Crustal
 contamination is minimal and fractional crystallization is the main process accounting for
 the geochemical and compositional variability of the rocks. The Creporizão Intrusive Suite
 (CRP) and synchronous rhyolites are products of this phase of arc-magmatism (Fig. 13a).
- As the arc evolves and the slab flattens, the mantle wedge is progressively metasomatized and eventually melts, generating the high-K to shoshonitic, metaluminous to mildly peraluminous rocks of the Parauari Intrusive Suite (PAR), representing the onset of the younger magmatic sequence (YMS), characterized by more evolved εNd_(1.88), under a lateto post-orogenic tectonic setting at ca. 1.89 Ga (Fig. 13b). The first pulses of the Iriri Group volcanism also form at this stage.
- After the flat-subduction event (Fig. 13c) and upon slab break off at ca. 1.87 Ga, melting
 preferentially occurred in the metasomatized SCLM, generating the shoshonitic
 Maloquinha Intrusive Suite (MLQ) and the last stages of the Iriri Group volcanism. Both
 units show geochemical characteristics that are diagnostic of changes of the tectonic

setting in the TMP, from a mature-arc and post-orogenic to an early-anorogenic setting, where originally metaluminous mantle melts became peraluminous through crustal assimilation (Fig. 13d). Fractional crystallization alone cannot account for the geochemical characteristics of rocks formed at that stage.

With respect to the potential for the formation of magmatic-hydrothermal mineral deposits, the first stage of the OMS, at 1.99 Ga, is characterized by a strong crustal component and a dry petrologic evolution (pyroxene bearing) that translates into weak metallogenetic potential. The transition to evolved arc (YMS) and late-orogenic settings (from 1.95 to 1.89 Ga), is accompanied by changes in the geochemistry of the igneous suites towards hydrous and oxidized conditions that render them metallogenetically favorable. Hence, part of CRP and PAR suites should be considered as potentially fertile for the formation of magmatic-hydrothermal deposits such as porphyry Cu-Au (Mo) and epithermal systems. Ultimately, the younger magmatic events might also act remobilizing or incorporating sulfides formed on the previous magmatic events, accounting for the existence of many Au-only magmatic-hydrothermal deposits at the TMP.

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