UNIVERSIDADE DE SÃO PAULO

INSTITUTO DE GEOCIÊNCIAS

The crustal assimilation in alkaline basic magmas: The Ponte Nova mafic-ultramafic massif and dikes/plugs of the Mantiqueira Range (SP-MG), Brazil

Mariana Robertti Ambrosio

Orientador: Prof. Dr. Rogério Guitarrari Azzone

TESE DE DOUTORAMENTO

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Mariana Robertti Ambrosio

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"The crustal assimilation in alkaline basic magmas: the Ponte Nova mafic-ultramafic massif and dikes/plugs from the Mantiqueira Range (SP-MG), Brazil "

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Abstract

This study aimed to investigate the impact of crustal assimilation on the SiO₂undersaturated Cretaceous alkaline rocks emplaced in the Mantiqueira mountain range in the northern sector of the Serra do Mar alkaline Province, southeastern Brazil. The focus was the most contaminated intrusions of the Ponte Nova alkaline massif, PNAM, the cumulate western intrusion (WI) and the porphyritic southern satellite intrusion (SSA), as well as the nearby basic/intermediate dikes and plugs. The study of disequilibrium textures, mineral chemistry and Sr isotope ratio in plagioclase and alkali feldspar crystals were employed to infer the processes occurred in different stages of magma evolution of PNAM in shallow crustal depths. The mineral isotope analyses were carried out using polytetrafluoroethylene filter and holder device to combine Laser Ablation (LA) as the sampling technique with Thermal Ionization Mass Spectrometry (TIMS). The chemical patterns observed in crystals were interpreted as the effect of AFC in the main stage of the evolution and the competition between AFC and magma recharge in the following stage. The sharp transition between core and rim of feldspar crystals and the disequilibrium textures of the respective cores reinforce mainly the abrupt chemical change of the system during their crystallization. SSA (represented by nepheline-bearing monzogabbros and nephelinebearing melamonzonites) may represent a magma recharge that came after the SSA-nph-mz (nepheline-bearing monzonites) emplacement, however the intrusion did not achieve the complete homogeneity as the petrographic and chemical data indicate. Assimilation of partial melt of crustal xenoliths and from the wall rock were pointed out as two mechanisms responsible for the PNAM contamination in agreement with previous studies. According to the results of modeling by Magma Chamber Simulator (MCS), the presence of Ba-rich minerals in the PNAM, especially Ba-rich feldspars, may be resultant of extensive fractional crystallization of enriched primitive melts and increase of SiO₂ activity by crustal assimilation. The patterns of Ba and Sr composition observed in plagioclase corresponds to those simulated using $log D_{Ba \text{ or } Sr}^{pl/melt}$ as a function of 1/T rather than constant coefficient values. The degree of scattering of trace element data in the analyzed crystals may be related to the disequilibrium crystallization and chemical heterogeneities in the magma chamber.

The studied basic/intermediate dikes and plugs varies from phonotephrite to tephriphonolite or trachyandesite to trachyte. The interaction of them with the acid wall rock in shallow depth of the crust is observed by their sinuous contacts and the presence of rounded crustal xenolith hosted in the alkaline rocks. The dikes and plugs are emplaced mainly in Precambrian batholith of Serra da Água Limpa and subordinately in the PNAM or in the medium-grained hololeucogranite which age (579.5 Ma) was obtained with U-Pb dating of zircon crystals. The occurrence of (open or closed) monomineralic or polymineralic

glomerocrysts in dikes and plugs suggests that magmas were stored in a magma chamber environment before ascending. Major- and trace-element contents of whole rock show that the magmas passed by extensive fractional crystallization of mafic minerals before reaching the shallower depth of the crust. The data fall in the field limited by magma mixing curves (basanite x silicic melts) constructed with ratios of highly incompatible elements (e.g., Nb/Pb, Th/Pb x Rb/Sr) or isotopes ((⁸⁷Sr/⁸⁶Sr)_i x (¹⁴³Nd/¹⁴⁴Nd)_i). AFC modeled by thermodynamic software (MCS) starting with a basanite magma supports that the crustal contamination has taken place mainly in upper crust (granitoid) where the partial melting could be greater under specific circumstances (e.g., earlier crustal heating, steep geotherm) rather than in lower crust (granulite). Likewise, part of data for major element oxides lies on the field formed with AFC and FC/magma mixing curves obtained by MCS. On other hand, AFC curves constructed using trace-element ratios (e.g., Nb/Pb, Th/Pb) do not reach most sample data likely due to the effect of mineral crystallization on the ratios used and the model uncertainties added in the selection of starting composition of the subsystems (main magma and wall rock) and trace-element partition coefficients. This study proposes that the crustal assimilation of dikes and plugs may have occurred during the magma ascent and possibly in a magma chamber in the upper crust. Among the factors that may have caused the lower level of crustal contamination of dikes and plugs compared to that found in WI and SSA/SSA-mz, it is cited the laminar regime of magma flow, the presence of chilled margin and the lower time of contact between magma and wall rock.

Key Words: Crustal assimilation, Sr isotope analyses, Alkaline magmas, Thermodynamic model

Resumo

Este estudo investigou o impacto da contaminação crustal em rochas cretáceas alcalinas e subsaturadas em sílica intrudidas na Serra da Mantiqueira no setor norte da Província alcalina da Serra do Mar, no sudeste do Brasil. A investigação abordou as intrusões mais contaminadas do maciço alcalino Ponte Nova, PNAM, a intrusão cumulática do oeste (WI) e a área satélite porfirítica do sul (SSA), como também os diques a plugs básicos a intermediários intrudidos na região. O estudo textural, de química mineral e da razão isotópica de Sr em cristais de plagioclásio e feldspato alcalino foram empregados para inferir os processos ocorridos em diferentes estágios da evolução magmática de PNAM, alojado em uma região rasa da crosta. O método aplicado para as análises isotópicas dos minerais consistiu em armazenar o material amostrado por laser ablation (LA) em um filtro de politetrafluoretileno dentro de um suporte e analisar o material digerido por espectrometria de massa por ionização térmica (TIMS). Os padrões químicos observados em cristais foram interpretados como efeitos de AFC no principal estágio de evolução magmática das duas intrusões estudadas de PNAM e uma competição entre AFC e a recarga de magma no estágio seguinte. A transição abrupta entre o núcleo e a borda dos cristais de feldspato alcalino e a textura de desequilíbrio desses núcleos reforçam, principalmente, a mudança química repentina ocorrida nos sistemas estudados entre a cristalização das duas zonas. SSA, representado por monzogabros com nefelina a melamonzonitos com nefelina, consiste em uma recarga de magma máfico que sucedeu a colocação do SSA-nph-mz (monzonitos com nefelina), entretanto, não houve a mistura completa entre os dois eventos intrusivos de acordo com a interpretação realizada por meio da petrografia e dos dados químicos dos minerais. A assimilação da fusão parcial de xenólitos crustais e da parede da encaixante são apontados como os dois mecanismos responsáveis pela contaminação crustal no PNAM, corroborando com estudos prévios. De acordo com os resultados da simulação realizada com o software Magma Chamber Simulator (MCS), a presença de minerais ricos em Ba no PNAM pode ser resultante da elevada cristalização fracionada do magma primitivo e do aumento da atividade de SiO₂ pela assimilação crustal. Os padrões da variação composicional de Ba e Sr observados nos cristais de plagioclásio correspondem aos respectivos padrões simulados pelo uso da relação de log $D_{Ba \, or \, Sr}^{pl/fundido}$ em função d 1/T em vez de valores constantes de coeficiente de partição. O grau de dispersão nos dados de elementos-traço nos cristais analisados deve estar relacionado à cristalização fora da condição de equilíbrio e à heterogeneidade da câmara magmática.

Os diques e os *plugs* variam entre fonotefrito e tefrifonolito ou entre traquiandesito e traquito. A interação deles com a encaixante ácida em profundidade rasa da crosta é observada pelos contatos sinuosos e a presença de xenólitos crustais arredondados hospedados nas rochas alcalinas estudadas. Os digues e plugs intrudem, principalmente, o batólito Pré-Cambriano da Serra da Água Limpa e, subordinadamente, no PNAM ou no granito com granulação média do qual a idade (579.5 Ma) foi obtida pela datação U-Pb em grãos de zircão. A ocorrência de glomerocristais monominerálicos ou poliminerálicos (fechados ou abertos) sugere que os magmas estudados foram estocados em um reservatório de magma antes da sua ascensão na crosta até a colocação. Conteúdos de elementos maiores e traços na rocha total mostram que os magmas passaram por um elevado fracionamento cristalino de minerais máficos antes de alcançar uma profundidade mais rasa da crosta. Os dados se inserem no limite do campo formado pelas curvas de mistura de magmas (basanítico x magma ácido) construídas com razões de elementos altamente incompatíveis (e.g., Nb/Pb, Th/Pb x Rb/Sr) ou de isótopos ((⁸⁷Sr/⁸⁶Sr)_i x (¹⁴³Nd/¹⁴⁴Nd)_i). O AFC modelado por um *software* termodinâmico (MCS) a partir do magma basanítico indica que a contaminação crustal ocorreu, principalmente, na crosta superior (granitoide) onde a fusão parcial é maior do que na crosta inferior (granulito) sob circunstâncias específicas como processos prévios de aquecimento da crosta. O campo composicional formado pelas curvas de AFC e FC/ mistura de magma obtidas por meio do software MCS se sobrepõe aos dados em óxidos de elementos maiores. Por outro lado, as curvas de AFC construídas usando razões de elementos-traço (e.g., Nb/Pb, Th/Pb) não atingem a maioria dos dados das amostras, possivelmente, devido ao efeito dos minerais cristalizados nas razões utilizadas e às incertezas do modelo aplicado relacionadas à seleção da composição inicial dos subsistemas (magma principal e encaixante) e do coeficiente de partição de elementos-traço. Este estudo sugere que a assimilação crustal dos diques e plugs deve ter ocorrida durante a ascensão do magma e, provavelmente, em uma câmara magmática na crosta superior. Entre os fatores que podem ter causado o nível mais baixo de assimilação crustal nos diques e plugs comparado àquele observado em WI e SSA/SSA-mz, podem ser citados o predomínio de um fluxo laminar de magma, a presença de margem resfriada no contato e o menor tempo de interação entre o magma e a encaixante.

Palavras-chave: Assimilação crustal, Análises isotópicas de Sr, Magmas alcalinos, Modelo termodinâmico

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1. Introduction

1.1 Justifications and goals

Alkaline rocks attract attention of researchers by their mineralogical diversity (Marks et al., 2011) and potential economical source (e.g., Biondi, 2005; Dostal, 2017; Mitchell, 2020). Another three significant aspects of alkaline rocks are their wide petrography and compositional variety, enrichment of incompatible elements (e.g., Morbidelli et al., 1995) and the low volume relative to the total crustal volume (Fitton and Upton, 1987). The petrogenesis of alkaline magmas has been intensively debated and it is highlighted two lines of researches that treat the alkaline magma generation or evolution. The first one has been focusing on their origin in the mantle. Assumptions based on the mantle xenoliths (e.g., Ackerman et al., 2013; Smart et al., 2019) and experimental studies (e.g., Pilet et al., 2008) have been supporting the models of melting of metasomatized lithospheric mantle to explain the alkaline melt origin. The low melting degree of garnet peridotite (Walter, 1998), the reaction between amphibole-rich veins and Iherzolite (Pilet et al., 2018) are two of the experiences that seek to explain the origin of basic to ultrabasic alkaline melts in the mantle. The second line of research is the investigation of processes responsible for the variety of rocks and alkaline magma compositions from ultramafic cumulate to more evolved rocks such syenites and phonolites, related to massif, suite or complex formations. The mentioned processes encompass fractional crystallization (e.g., Beccaluva et al., 1992; Gomes et al., 2017), magma mixing (e.g., Dowes, 1989; Araña et al., 1994) and crustal assimilation (Piochi et al., 2006; Melluso et al., 2018).

The central to southern part of the South America platform hosts more than 200 alkaline or alkaline-carbonatite massifs and complexes, with ages mainly from Early to Late Cretaceous and lasting to the Paleocene, and emplaced (Fig. 1) mainly along the margins of Paraná, Bauru, Santos and Pelotas basins, at rift system of Asunción, Cabo Frio lineament and Amazon craton (Gomes and Comin-Chiaramonti, 2005; Ricommini *et al.*, 2005). The region encompasses Brazil, Paraguay, Bolivia and Uruguay. The complexes are divided into 15 Provinces according to the tectonic settings and the Brazilian ones are related to the Early and Later Cretaceous and Paleocene (Ricommini *et al.*, 2005). The most abundant types are intrusive SiO₂-undersaturrated to saturated syenites (Ulbrich *et al.*, 2005; Gomes *et al.*, 2017; Rosa and Ruberti, 2018). The basic to ultrabasic types are emplaced chiefly as dikes, pipes and plugs (*e.g.*, Brotzu *et al.*

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Figure 1: Alkaline provinces of the central-southeastern region of the Brazilian Platform. 1) Late Ordovician to Early Cretaceous Paraná Basin; 2) Early Cretaceous tholeiitic lava flows; 3) Late Cretaceous Bauru Basin; 4) Offshore marginal basins; 5) alkaline provinces; 6) age of alkaline rocks (diamonds, Permian-Triassic; squares, Early Cretaceous; triangles, Late Cretaceous; circles, Paleogene); 7) Axes of main archs (AX, Alto Xingu; SV, São Vicente; BJ, Bom Jardim de Goiás; PG, Ponta Grossa; RG, Rio Grande; PP, Ponta Porã); 8) Torres Syncline; 9) Major fracture zones, in part deep lithospheric faults (Rifts: MR, Mercedes; RM, Rio das Mortes; MG, Moirão; SR, Santa Rosa; AR, Asunción; Lineaments: TB, Transbrasiliano; AP, Alto Paranaíba; MJ, Moji-Guaçu; CF, Cabo Frio; RT, Rio Tietê; SL, São Carlos-Leme; PR, Paranapanema; PI, Piedade; GP, Guapiara; JC, São Jerônimo-Curiúva; RA, Rio Alonzo; PQ, Rio Piquiri; AM, Santa Lucía-Aiguá-Merin). Mapa from Riccomini *et al.* (2005).

2005). The cumulate rocks are usually associated with carbonatite rocks (Beccaluva *et al.*, 1992; Beccaluva *et al.*, 2017; Chmyz *et al.*, 2017).

The effect of magma source in the mantle on alkaline/carbonatite bodies of Brazilian platform has been frequently discussed (e.g., Morbidelli et al., 1995; Gibson et al., 1995a, b; Traversa et al., 2001; Ruberti et al., 2012). Thompson et al. (1998) and Gibson et al. (1999) have suggested that the appearance of studied sodic and potassic melts with spatial and temporal association in Brazilian platform may be resultant of four variables as follow: 1) the composition of the mantle (*e.g.*, the metasomatized vein composition, stabilization of phlogopite by low F/H_2O ; 2) temperature; 3) the melting rate of mantle; 4) the depth of melting in the mantle that contributes to the stability of minerals such phlogopite and ilmenite that host K and Ti, respectively. However, the study of impact of crustal contamination on the magmatic evolution still deserves more investigation and even more in terms of the assimilation mechanisms. Among the published investigations or detection of open-system processes in alkaline/carbonatite magmas within the Brazilian territory, it is mentioned the studies on the Lages suite (Traversa et al., 1996), the Itatiaia alkaline complex (Brotzu et al., 1997), the dikes of Serra do Mar alkaline Province (Thompson et al., 1998; Azzone et al., 2018), the Cananéia massif (Spinelli and Gomes, 2009), the Ponte Nova ultramafic-mafic alkaline massif (Azzone et al., 2016; Azzone et al., 2020), the Jacupiranga alkaline complex (Roden et al., 1985; Chmyz et al., 2017), the José Fernandes suite (Almeida et al., 2019) and the Indaiá-II Kimberlite (Lima et al., 2020).

This study focused on understanding the mechanism of crustal contamination on the most contaminated intrusions of the Ponte Nova alkaline massif (PNAM; Azzone *et. al.*, 2009a) and basic/intermediate dikes and plugs located at the Mantiqueira mountain range at the northern sector of Serra do Mar alkaline Province, SE, Brazil. This sector comprises the alkaline complexes of coastline of northern São Paulo State and those emplaced in the Mantiqueira mountain range located in the limit among São Paulo, Minas Gerais and Rio de Janeiro states in the southeast of Brazilian platform (Fig. 2A). The structure and petrography of the PNAM were well-characterized in Azzone *et al.* (2009a). The massif consists of two areas where the largest one (~5.5 Km²) is formed mainly by cumulate gabbroic intrusions and the smallest one (~1 Km²), a southern satellite area (SSA), has porphyritic nepheline-bearing monzogabbros as the dominant rock and nepheline-bearing melamonzonites to monzonites (SSA-nph-mz) as subordinate rocks. The PNAM was formed in shallow depth of the crust by multiple pulses of crystal-laden potassic basanitic magmas (Azzone *et al.*, 2009a and 2016). The PNAM was chiefly

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Figure 2: A) The map of the Serra do Mar Alkaline Province at southern region of Brazil (modified from Thompson *et al.*, 1998). B) Map with localization of the Ponte Nova alkaline massif (PNMA) and dikes and plugs investigated (in light green symbols) in this study. Map modified from Azzone *et al.* (2016, 2018); Crystalline basement modified from Nunes *et al.* (2020).

emplaced in the Precambrian Serra da Água Limpa batholith (Vinagre *et al.*, 2014a, b). It is possible to distinguish seven intrusions in the largest area of the massif (Fig. 2B). The Western Intrusion (WI) and Central Intrusion (CI) are divided into lower (LS) and upper (US) sequences. The LS comprises mafic- ultramafic, meso- to orthocumulate coarse-grained rocks (clinopyroxenites and melagabbros), whereas the US consists of fine- to medium-grained porphyritic and inequigranular nepheline-bearing monzogabbros. The Northern Intrusion (NI) exhibits coarse-grained cumulate melagabbros and the Eastern Intrusion (EI) is formed by fine to medium-grained porphyritic nepheline-bearing monzogabbros to mozondiorites. Other three subordinate intrusions of the main region consist of CP (a small plug of porphyritic to equigranular micrograbbros), ICp (ilmenite clinopyroxenites and magnetitites) and Brc (magmatic breccia).

Azzone et al. (2016) have highlighted the importance of the crustal contamination plus fractional crystallization (AFC) on the magmatic evolution mainly in WI, SSA, EI by petrographic, geochemical, isotopic evidences and thermodynamic model (MELTS package - Ghiorso and Sack, 1995). Azzone et al. (2016) by observations of mineral textures and wide range of Sr isotope ratios in plagioclase and apatite of CI-LS, WI-LS, EI, NI and SSA have shown that the magma hybridization (partial melt of crustal rocks interacting with basanite magmas) took place in a shallow magma chamber environment. The thesis aimed to further comprehend the assimilation process of the most contaminated intrusions (WI-LS, WI-US, SSA/SSA-nph-mz) of the PNAM adopting three lines of investigation: 1) to track the Sr isotope ratio of magmatic evolution of each intrusion through analysis of plagioclase, core and rim of alkali feldspar crystals, *i.e.*, the sequence of crystallization; 2) to relate the mineral textures with additional chemical mineral data plus thermodynamic models to construct a model of magmatic evolution of WI-LS / WI-US and SSA-nph-mz / SSA; 3) to extend the discussion initiated in Azzone et al. (2016) about the contribution of partial melting of crustal xenolith and wall rock to the contamination of the targeted intrusions. In addition, alkali feldspar and biotite crystals with up to 9.2 and 7.3 mass % content of BaO, respectively, are mainly hosted in the most contaminated intrusions of the PNAM (WI, SSA/SSA-nph-mz). Similar high-Ba content has not been found in such crystals of other intrusions of the Serra do Mar alkaline Province. This unusual mineral composition has been related to the origin of PNAM magmas in enriched mantle (Azzone et al., 2009b). This thesis extended the debate of the origin of Ba-high content of the PNAM melts by the examination of the Sr isotope data of Ba- rich alkali feldspar and major- and trace-element modeling.

The dikes and plugs of northern sector of Serra do Mar alkaline Province emplaced in the Precambrian Ribeira mobile belt or crosscut alkaline intrusions. They range from centimeters to some meters in width. According to Brotzu et al. (2005), the dikes are classified in strongly SiO₂- undersaturated suite (foidite-phonolite) or weakly SiO₂undersaturated suite (alkali basalts-trachyte). Azzone et al. (2018) grouped the dikes hosted in Mantiqueira mountain range in three alkaline series based on the normative nepheline (*ne*) content, (the weakly SiO₂-undersaturated series: normative ne < 7; potassic intermediate series: 7 < normative *ne* < 13; sodic, strongly SiO₂-undersaturated series: normative ne > 13). The wide compositional variety of more primitive dikes of the Serra do Mar alkaline Province has been related to the mantle heterogeneity (Azzone et al., 2018). On other hand, Menezes et al. (2015), Ambrosio and Azzone (2018) and Lopes et al. (2020) have recognized the presence of xenocrysts and/or antecrysts and the impact of them on the bulk composition of basic porphyritic alkaline dikes of the studied region. Lopes et al. (2020) have associated the presence of mantle xenocrysts and complex zoned antecrysts in alkaline dikes of Mantiqueira mountain range with opensystem processes such as assimilation and magma mixing in previous magmatic stages in depth. Crustal contamination is also recognized by variation of Sr and Nd isotope ratios in picrites (Thompson et al., 1998) and more evolved compositions or weakly SiO₂undersaturated series (Azzone et al., 2018). The contribution of the second part of this study is dedicated to the measurement of crustal assimilation on basic/intermediate dikes and plugs of Mantiqueira range and the investigation of assimilation mechanisms based on field evidence, mineral textures, bulk composition and mass-balance and thermodynamic modeling. The selected dikes and plugs (Fig. 2B) are included in both suites designated by Brotzu et al. (2005), whereas most of them are included in the potassic weakly silica-undersaturated series or in the potassic intermediate series of Azzone et al. (2018).

1.2 Strategies

Firstly, this study investigated the level of contamination experienced by the two most contaminated intrusions of the massif (WI and SSA/SSA-nph-mz) using mineral chemistry (major and trace elements) and Sr isotope ratio in plagioclase and alkali feldspar. The textural analysis and chemical data from plagioclase crystals, cores and rims of alkali feldspar and biotite crystals were employed to infer the possible processes occurred in different stages of the magma evolution. Also supported by the textural analysis and chemical data of partial melted/digested crustal xenoliths and of minerals crystallized from highly hybridized melt, it was evaluated the role of the known mechanisms of crustal contamination on the magmatic evolution of the PNAM. The effect of AFC on the liquid line of descent of the main magma was estimated with thermodynamic package (Magma Chamber Simulator – MCS - Bohrson *et al.*, 2014; 2020). The origin of high content of Ba in the massif, expressed in alkali feldspar and biotite crystals enriched in Ba, was debated taking into account the trace-element modeling performed with MCS.

The interpretation of whole-rock composition and the mass-balance and thermodynamic models were the main adopted strategies to evaluate the impact of crustal contamination on the magmatic evolution of basic/intermediate dikes and plugs. Fractional crystallization (FC), assimilation plus fractional crystallization (AFC), magma mixing and FC + magma mixing were modeled and the obtained trends were compared with the trends of major and trace elements and Sr, Nd isotope signatures of the dikes and plugs. The textural study of macrocrysts hosted in the rocks allowed to infer some magmatic processes that took place during magma trajectory within the crust. Furthermore, the field aspect of the contacts between dikes or plugs and country rock contributed to understand the assimilation mechanism at emplacement stage. The radiometric dating of zircon grains of the granitic country rock of two of the studied dikes aided to verify whether the granitic emplacement was recent enough to increase the local thermal gradient and produce the field observations. Additionally, the use of MCS was important to analyze the melting potential of the crust under different depths, the effect of thermal gradient of the crust on the melting rate.

This research project entitled *The crustal assimilation in alkaline basic magmas: The Ponte Nova mafic-ultramafic massif (SP-MG)* was developed by Mariana Robertti Ambrosio under doctor Rogério Guitarrari Azzone's supervision at the Institute of Geoscience (IGc) of University of São Paulo (USP). The IGc provided laboratory support services such as sample treatment laboratory, microscopy imaging laboratory (polarized light microscopy, scanning electron microscopy), chemical analysis laboratory (whole-rock analysis: X-ray fluorescence spectrometry, multi collector inductively coupled plasma mass spectrometry). In addition to the laboratory facilities cited above, the electron microprobe laboratory of UNESP of Rio Claro, chemical analysis laboratory (*whole-rock* analysis: inductively coupled plasma mass spectrometry), radiometric dating laboratory (laser ablation multi collector inductively coupled plasma mass spectrometry).

of UNICAMP were used. The doctoral student was supported by Coordination for the Improvement of Higher Education Personnel (CAPES) in Brazil and the national and international chemical analyses by São Paulo Research Foundation (FAPESP, process number: 2012/06082-6; 2017/03768-8). For this study purpose, the doctoral student developed the research project entitled Sr and Pb in-situ isotopic analyses in minerals from the Ponte Nova mafic-ultramafic alkaline massif (SP-MG): the study of mechanisms of crustal contamination in shallow-level magma chambers at College of Earth, Ocean, Atmospheric Sciences of Oregon State University (OSU). The project was supervised by doctor Frank J. Tepley III of OSU and doctor Rogério G. Azzone of USP with the participation of doctor Frank Ramos (New Mexico State University, NMSU). The Interuniversity Exchange Doctoral Scholarship was funded by National Council for Scientific and Technological Development (CNPg, process number: 205705/2018-9, duration: 5-1-2019 to 4-31-2020). The sampling procedure of crystals and crystalline zones was carried out at laboratory facility of College of Earth, Ocean and Atmospheric Sciences at Oregon State University. The sample digestion/chromatography step and analyses by Thermal Ionization Mass Spectrometry (TIMS) were performed at Geological Sciences Department at NMSU. Doctor Frank J. Tepley III and doctor Frank Ramos guided the Mariana's activities in the laboratory. It is worth mentioning that this study was the first work to employ the filter and holder device to combine LA as the sampling technique with the analytical technique TIMS in isotope ratio analyses of mineral. Marie Katherine Takach, doctor Wendy Bohrson's former student and current PhD candidate of OSU, contributed to the discussion of MCS software use in this study.

To report the obtained data and respective discussions, beside the current chapter (*Introduction*), the thesis was segmented in four additional chapters. The *Methods* encompasses the analytical procedure of sample analyses, the procedure adopted to the data treatment and the descriptions of mass-balance and thermodynamic models. The third and fourth chapters correspond to the study of magmatic processes of the PNAM (*The elemental and Sr isotope fingerprints in minerals to study the impact of open-system processes on a shallow magma chamber, the Ponte Nova alkaline massif, SE, Brazil)* and basic/intermediate dikes and plugs (*The contribution of different Neoproterozoic country rocks on the evolution of Cretaceous alkaline dikes from the Mantiqueira range*), respectively. Both chapters (3 and 4) were written in scientific journal style. The fifth chapter (*Integrated Discussion and final remarks*) summarizes the results achieved in this thesis and points the challenges, advantages and drawbacks of the analytical and modeling methods employed in this study. Finally, the *Supplementary Material* section

hosts the data tables, output files of MCS and supporting materials for further variable calculations and data used in models.

1.3. References

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2. Materials and methods

This chapter presents the analytical methods employed to analyze whole-rock samples and minerals for major-, minor- and trace-element composition and isotope ratios. The data treatment procedure adopted is also detailed. This text consists of an extended version of the brief method descriptions presented in Chapters 3 and 4. Moreover, it describes the mass-balance and thermodynamic models and their variables used in this study.

2.1 Sample, sample preparation and analytical methods

Samples of the PNAM and nearby dikes/plugs (Mantiqueira Range) were collected in previous research projects (FAPESP – Process numbers: 03/00626-5 and 2010/20425-8). For the development of this study, samples were selected mainly from SSA/SSA- nphmz and low to high topographic level of WI (WI-LS and WI-US) and from EI, trying to find the most contaminated samples and minerals from the massif and dealing with crustal xenoliths in thin sections. Also, dikes and plugs nearby PNMA were systematically sampled to obtain representative samples of their zones. The localization and sample number are indicated in Chapters 3 and 4. From 16 samples of dikes/plugs and country rocks, 18 thin sections and 2 polished thin sections were produced and 19 whole-rock analyses were carried out taking into account the number of replicates of two samples. About 28 samples from diverse intrusions of the PNAM (CI, WI, EI, SSA, SSA-nph-mz, NI, CP) were handled to produce 31 thin sections plus their respective polished thin sections.

2.1.1 Whole-rock analyses

The samples of dikes and plugs were sawed to remove weathering parts. The thick slices of fresh samples were directed to the preparation of polished thin sections or the sample treatment for chemical analyses. The milling process of samples followed Sertek *et al.* (2015). It was used hydraulic press with stainless steel plates and agate ring mill to pulverize 0.5 - 1 kg samples. The quartering method was employed in the resulting powder. After measuring of loss on ignition, fused glass disc was prepared using 1 g of sample and 9 g of lithium metaborate:lithium tetraborate commercial flux (2:1) to determinate major and minor elements by X-ray fluorescence spectrometer,

XRF(PANalytical, AXIOS MAX Advanced) at NAP GeoAnalítica-USP Core Facility (see Mori *et al.* (1999) for further details on disc preparation and analysis). The JB 1a and JG 1a were used as reference material for the quality control of analyses.

Trace-element determination was carried out at Geochemistry Laboratory of DPCT-UNICAMP Facility. For the analysis, 40 mg of powdered sample were digested in analytical-grade acid solution (HNO₃ + HF) with microwave acid digestion bomb and analyzed by inductively coupled plasma mass spectrometry - ICP-MS - XSeriesII (Thermo) equipped with CCT (Collision Cell Technology). The operating conditions used were nebulizer Ar flow (0.81 – 0.85 L/min), plasma Ar flow (13 L/min), and ICP RF power (1400 W). H₂ (7 %) in He was used in collision cell to remove isobaric interference on ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn. The instrument calibration took place with multi-element solutions prepared with single calibration standards (SCP Science) by gravimetric method. The polyatomic interferences were corrected mathematically. The quality control was made with BRP-1 reference material. The method adopted was based on Navarro *et al.* (2008).

The Sr and Nd isotope ratios were obtained by Thermal Ionization Mass Spectrometry - TIMS (Thermo Scientific TRITON) - with average of 100 cycles of analyses per sample at CPGeo – USP facility. The powdered sample (50 mg) was digested in acid solution (HNO₃ + HF + HCl) in a hotplate and the resulting solution were purified by chromatography step according to Magdaleno et al. (2017). Sr was first separated using Spec resin (Eichrom®) and Nd was separated using Ln resin (Eichrom®) from the discarded solution of previous chromatography step. The chemical treatment took place in a class 10,000 cleanroom. The resulting solutions were loaded on the single Ta filament and double Re filaments for Sr and Nd isotope analyses, respectively. The instrumental mass discrimination was corrected with exponential law using ⁸⁶Sr/⁸⁸Sr = 0.1194 (Nier, 1938) and 146 Nd/ 144 Nd = 0.7219 (DePaolo, 1981a). The blank analysis yielded 87 pg of Sr and 64 pg of Nd. The age correction on the obtained ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd values was made with t (time) value of 85.4 Ma (Azzone et al., 2018). The main values of reference material obtained from April/2019 to March/2020 were 0.710268 ± 0.000015 (NIST SRM 987 = 0.710252 ± 0.000013; Weis *et al.*, 2006) for ⁸⁷Sr/⁸⁶Sr and 0.512107 ± 0.000003 (JNdi-1 = 0.512115 ± 0.000007; Tanaka *et at.*, 2000) for ¹⁴³Nd/¹⁴⁴Nd. The blank and solutions used for trace-element or isotope ratio determination were prepared with low-resistivity deionized water (18.2 MΩ.cm at 25 °C) produced in the Milli-Q[®] Plus system. The analysis results of samples and reference materials as the limit of detection values are reported in the Supplementary material (Tables 1S-3S).

2.1.2 U-Pb dating of zircons

The zircon crystals of MRGA-1 (granite) were extracted from rock matrix by standard mineral separation techniques following the procedure described in Sato et al. (2014) at CPGeo – USP facility and fixed in an epoxy resin mount at NAP GeoAnalítica-USP Core Facility. It was used jaw crusher, disc mill, sieving, Wilffley table, isodynamic Frantz separator and heavy liquids. Polished crystals in the mount were analyzed for U-Pb isotope dating with laser ablation sector field inductively coupled plasma mass spectrometry (Thermo Scientific, Element XR) at Isotope Geology Laboratory -UNICAMP. For this purpose, 42 inclusion-free rims and the intermediate zones of crystals were selected for analyses. The laser ablation system consisted of Photon Machine (Excite 193) in two volume cell HeIEX. Its ablation settings were laser beam of 25µm, fluency of 9 J.cm⁻², repetition rate of 10 Hz, ablation duration of 40 secs. He carrier gas (100%) of 0.6 L.min⁻¹ in MFC 1 and 0.7 L.min⁻¹ in MFC 2. The masses measured were 202, 204, 206, 207, 208, 235 and 238 in 4 ms each one. The gas blank influence was discounted by subtracting the result of 20-sec on-peak zero analysis. The calibration was made with 91500 zircon (Wiedenbeck et al., 1995) and the quality control with zircon of Tocantins (Brazil) (in preparation) and Plešovice zircon (Sláma et al., 2008). The laserinduced elemental fractionation corrected by normalization to reference material, the correction of instrumental mass discrimination and the isobaric interference were made by lolite[™] software. The data are presented in Supplementary material (Tables 4S, 5S, Fig. 1S) and additional information about the age calculation and quality of analyses are found in Section 2.2.

2.1.3 Major- and minor- element analyses in minerals

Petrographic study was carried out in 100-µm polished thin sections of samples from WI, SSA/SSA-nph-mz, EI, CI nad NI and MRGA area (see Chapters 3 and 4 for sample localization). Optical and scanning electron microscope (SEM) were used to identify chemical zoning, resorption features and mineral inclusion in target phases (plagioclase, alkali feldspar, biotite, clinopyroxene). The use of SEM took place at Technological Characterization laboratory of Polytechnic Institute – USP and at the SEM laboratory of Geosciences Institute – USP. After performing the petrographic study, the polished thin sections were cleaned with distilled water in an ultrasound bath, dried and coated with a thin layer of carbon. The minerals were analyzed by electron microprobe

(EMP) (JEOL, JXA-FE-8530) at the GeoAnalítica-USP Core Facility equipped with a Schottky field emission (FE) electron gun, five wavelength-dispersive X-ray spectrometers (WDS), one energy-dispersive X-ray spectrometer (ED), ten analyzer crystals and luminescence sensor (LS). Part of analyses was also performed using EMP (JEOL, JXA-8230) at EMP laboratory of Geosciences Institute – UNESP equipped with five WDS, one EDS, ten analyzer crystals and LS. The equipment was set up with 5-15µm electron beam, current of 20 nA and accelerating voltage of 15 kV. The matrix effect was corrected by the PZR Armstrong algorithm using PROZA software (Bastin and Heijligers, 1990). The reference materials used in calibration of the EMP and the diameter size of electron beam are presented in Table 6S. The major- and minor- (Ba, Sr) element determination in feldspars of MRGA-2b dike were made at laboratory facility of College of Earth, Ocean and Atmospheric Sciences at Oregon State University. The minerals were analyzed by Cameca SX-100 Electron Microprobe equipped with 5 WDS and one EDS with thin window for light element detection. The instrument was set up with electron beam diameter of 5 µm, current of 30 nA and accelerating voltage of 15 kV. The compositional tables for major elements in oxide (mass %) in minerals are shown in Supplementary material (Tables 7S-11S).

2.1.4 Trace-element analysis in minerals

Trace elements in plagioclase, alkali feldspar and biotite from samples of WI, SSA/SSA-nph-mz and EI were determined by inductively coupled plasma mass spectrometer, ICP-MS (Thermo Scientific, ICAP Q), with a laser ablation system (UP-231/AF, New Wave) attached. The Nd:YAG laser (Tempest, Eolite) with a 213 nm wavelength was operated in Q-switched mode. The carrier gas was a mixture of Ar (0.58 L.min⁻¹) and He (0.60 L.min⁻¹). The operating conditions of the laser ablation system are presented in Table 1 for each mineral phase. The mass spectrometer is equipped with a single quadrupole and a collision/reaction cell. Some of operating conditions were nebulizer gas flow (1.01 L.min⁻¹), auxiliary gas flow (1 L.min⁻¹), plasma gas flow (16 L.min⁻¹), lens voltage (7 V) and ICP RF power (1100 W). Areas already analyzed with the EMP or equivalent regions were targeted by laser ablation. The reference material for instrument calibration was analyzed twice before starting the analysis of a type of mineral and after the last analysis of the same mineral of the respective polished thin section. After performing six consecutive mineral analyses, the reference material analysis was also repeated for calibration purpose. Another reference material was used to check the

analytical routine performance for each mineral phase analyzed in each polished thin section. The reference material used for instrument calibration and quality control of method employed are presented in Table 1. The blank and the analysis were obtained within 40 and 60s, respectively. The data acquisition was processed within Thermo Scientific[™] Qtegra[™] Intelligent Scientific Data Solution[™] (ISDS) software and the data reduction was carried out with the software Glitter®, developed by GEMOC (Access MacQuarie Ltd). The Ca and Si content obtained in EMP analysis were used as an internal standard for clinopyroxene and further minerals, respectively. The mean value of the limit of quantification and the result of reference material analyses are shown in Tables 12S and 13S, respectively.

Table 1: Operating conditions of the laser system, reference materials (RM) used for spectrometer calibration and quality control of the routine used for mineral analyses by ICP-MS. Abbreviations: Plagioclase (PI), Alkali feldspar (Afs), Biotite (Bt), Clinopyroxene (Cpx).

	PI	Afs	Bt	Срх	
Laser repeat rate/Hz	15	15	15	12	
Laser power/ %	80	80	75	80	
Diameter/µm	80 (spot)	80 (spot)	40 (raster)	55(spot)	
Speed/µm.s ⁻¹	-	-	2	-	
RM (calibration)	Nist 612	Nist 612	Nist 610	BHVO-2G	
RM (control)	BHVO-2G	BHVO-2G	BHVO-2G	Nist 612	

2.1.5 Sr isotope analysis in plagioclase, alkali feldspar and clinopyroxene

The plagioclase crystals, alkali feldspar zones and augite crystals were sampling using Analyte G2 excimer equipped with a HelEx II cell (Teledyne CETAC Technologies, USA) at laboratory facility of the College of Earth, Ocean and Atmospheric Sciences at Oregon State University. The 93-nm laser beam was used with diameter of 120 μ m, repetition rate of 15 Hz, energy fluence of 6.35 J.cm⁻² and 75% of the power. The laser was employed in the raster mode with rate of 5 μ m.s⁻¹ from 3 to 9 min. The ablated material was transported from the laser device cell by He carrier gas (0.85 L.min⁻¹) to a polytetrafluoroethylene (Teflon) filter (0.45 μ m pore size, Pall) confined in a holder. The filter with the ablated sample was kept in a Teflon beaker. The schematic diagram of the experimental set-up is shown in Fig. 3.

The sample preparation and microanalyses were made at Geological Sciences Department at New Mexico State University based on Wolff *et al.* (1999). The acid digestion of the samples and chromatography were made at a clean room. The filter with the mineral powder was immersed into 1.5 ml of concentrated HF-HNO₃ mixture (2:1) V.V⁻¹ and heated on a hotplate for two days in sealed Teflon digestion vessel. The filter was removed and the solution was dried. The material obtained was dissolved with 6 N HCl and dried again on the hot plate. In order to load on the chromatographic column, the dried material was re-dissolved with 50 μ L of 2.5 N HCl. The cation exchange chromatography to separate Sr from Rb was carried out using glass column filled with AG[®] 50W-X8 of 200-400 mesh (Bio Rad). The sequence of solvent added to the column and eluted solution is shown in the Table 2. Each eluate was dried on the hotplate and the residue was re-dissolved with 50 μ L of 2.5 N HCl during one day under heating to be loaded onto a single rhenium filament. The same procedure employed in the samples were made with blank and standard. Deionized water was used to make acid solution and to aid chromatographic columns filling. Teflon beakers, chromatographic resin and column were cleaned with 6.0N HCl solution before the procedure. The acids were of high purity and/or doubly distilled before the use.

Step	Prepare	Load	Wash	Wash	Wash	Collect	Wash	Collect	Clean
	Column								column
Eluent	2.5N	2.5N	2.5N	2.5N	2.5N	2.5N	2.5N	2.5N	6.0N
	HCI	HCI	HCI	HCI	HCI	HCI	HCI	HCI	HCI
Volume	2000	50	50	50	100	700	350	700	
/ μL									
Eluate						Rb		Sr	

Table 2: Chromatographic steps to separate Rb and Sr from solution of digested microsample.

The Sr isotope ratios were obtained by TIMS, Thermal Ionization Mass Spectrometry (VG Sector 54, UK). The equipment has seven Faradays cups and one ioncounting Daly photomultiplier. The single rhenium filament was degassing under high temperature and vacuum conditions. A slurry of Ta_2O_5 made with 2% $TaCl_5$, 1% H_3PO_4 , 1% HF, 12% HNO₃ by weight in water (Birck, 1986) used as activator was deposited onto the filament and dried prior to the sample load. The filament with the sample load was dried before being inserted into the equipment. The ratio determinations were made in peak-hopping mode and the pressure of equipment varied between 10⁻⁶ and 10⁻⁷ bar. The isotope analysis results are in Chapter 3 and the calculation of Sr ratio is described in section 2.2.



Figure 3: Schematic diagram of analytical method employed to determine Sr isotope ratios in crystals or crystalline zones of plagioclase or alkali feldspar from samples of WI and SSA/SSA-nph-mz from the PNAM. The crystal is sampled using laser ablation system and the material is transported to a PTFE filter by He gas carrier. The filter plus sampled material is immersed in a mix of concentrated acids under heating to dissolve the sample. The digested sample is purified by chromatography to obtain Sr purified solution, *i.e.*, sample-matrix-free solution. The purified solution is analyzed by TIMS to determine ⁸⁷Sr/⁸⁶Sr and ⁸⁴Sr/⁸⁶Sr. Sample treatment and isotope analyses were based on Wolff *et al.* (1999).

2.2 Data treatment and quality control of analyses

For all chemical results, only mass fraction (mass % or ppm) above the limit of quantification (~3.3 x limit of detection - Potts, 1987) was considered (Tables 1S, 2S, 6S, 12S). Mineral inclusions sampled by ablation process in trace element analyses were removed from the whole time-resolved analysis using Glitter software. Only trace element analyses with ablation time above 30 s were accepted. Most of the results obtained from analyses of reference materials to control the quality of the method employed overlap the known value interval (Table 1S, 2S, 13S, 3.5.5 and Fig.25). It was also reported the relative deviation standard (RSD) for trace element analyses according to the expression ($2\sigma \times 100$)/a where σ is the internal precision of the analysis and a is the content of the trace element. Trace elements in lower concentration have higher RSD, thus it was needed to evaluate the σ values mainly when these lower concentrated elements were used to develop the study.

During the isotope analyses of the microsamples, the current of the filament was controlled to make longer the ion emission. In addition, the absent signal of Rb was also checked during the initial heating of sample-loaded filament in TIMS to certify the quality of chromatography separation. The signal intensity of ⁸⁸Sr achieved around 3V and this value was kept for more than 100 readings during the analyses of zones ablated for more than 7 min. The internal error on the ⁸⁷Sr/⁸⁶Sr ratio ranged between 0.002 and 0.01 % (2σ SE). The mass fractionation was corrected using the exponential law with the value of 0.1194 for ⁸⁶Sr/⁸⁸Sr according to the equation (1), where M is the isotope mass (Pearson *et al.*, 2008).

$$\left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_{\text{true or corrected}} = \left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_{\text{measured}} \times \left(\frac{{}^{M}_{87}{}_{\text{Sr}}}{{}^{M}_{86}{}_{\text{Sr}}}\right)^{\beta}$$
(1)

Where
$$\beta = \frac{\ln \left[\frac{0.1194}{\left(\frac{86}{88}\text{sr}\right)_{\text{measured}}}\right]}{\ln \left(\frac{M_{86}\text{sr}}{M_{88}\text{sr}}\right)}$$

To obtain the initial ratio of ⁸⁷Sr/⁸⁶Sr, the fundamental equation of geochronology was employed (2).

$$\binom{{}^{87}Sr}{{}^{86}Sr}_{initial} = \binom{{}^{87}Sr}{{}^{86}Sr}_{Measured} - \binom{{}^{87}Rb}{{}^{86}Sr}_{Measured} \left(e^{\lambda t} - 1\right)$$
(2)

Where λ (decay constant) = 1.42 x 10⁻¹¹ / years (Faure and Mensing, 2005) and t = 87.6 x 10⁶ years (Azzone *et al.*, 2016). For simplicity, the $\frac{{}^{87}Rb}{{}^{86}Sr}$ ratio is approximated to $\frac{Rb x {}^{87}Rb abundance x atomic mass of Sr}{Sr x {}^{86}Sr abundance x atomic mass of Rb}$ ratio with $\frac{Rb}{Sr}$ obtained by LA-ICP-MS analysis.

The accuracy or performance of the analytical technique for isotope analysis in plagioclase and alkali feldspar was checked out by the analysis of reference material (NIST, SRM 987), the analytical blank (see Chapter 3) and the $\frac{^{84}Sr}{^{86}Sr}$ value of each analysis. The measured $\frac{^{84}Sr}{^{86}Sr}$ ratios agree with the accepted value of 0.0565 (Thirwall, 1991) for most data (Fig. 4). The $\frac{^{84}Sr}{^{86}Sr}$ values from analyses by TIMS are less spread and more accurate than those obtained by LA-MC-ICP-MS, but that was just as expected once the isobaric interferences such as 87 Rb on 87 Sr are eliminated by chromatographic separation.

In addition, analyses by TIMS do not generate molecular interference such as Ca argides (*e.g.,* ⁴⁸Ca³⁶Ar, ⁴⁶Ca³⁸Ar, ⁴⁴Ca⁴⁰Ar) detected in analyses of Ca-rich samples by LA-MC-ICP-MS (Vroon *et al.*, 2008), for example. As the range of $\binom{^{87}Sr}{^{86}Sr}_{initial}$ ratios from Azzone *et al.* (2016) overlaps the values obtained in this study, data from Azzone *et al.* (2016) were also used in the development of the discussion (Chapter 3).



■ This study ▲ Azzone et al. (2016)

Figure 4: Evaluation of the analytical accuracy using ⁸⁴Sr/⁸⁸Sr ratios of plagioclase and alkali feldspar analyses by TIMS (this study) and ⁸⁴Sr/⁸⁸Sr ratios in plagioclase by LA-MC-ICP-MS from Azzone *et al.*(2016). The obtained results are compared with the accepted value of Thirwall (1991).

The age estimative of zircon crystallization were carried out with the U-Pb concordia plot (Wetherill's concordia - Wetherill, 1956). The Wetherill's concordia consists of a graphical procedure constructed using the equations (3) in Y-axis and (4) in X-axis.

$$\frac{{}^{206}\text{Pb}*}{{}^{238}\text{U}} = e^{\lambda_1 t} - 1$$
(3)

$$\frac{{}^{207}\text{Pb}*}{{}^{235}\text{U}} = e^{\lambda_2 t} - 1$$
(4)

Where λ_1 (=1.55 x 10⁻¹⁰ / years) and λ_2 (9.8 x 10⁻¹⁰ / years) correspond to the decay constant of ²³⁸U and ²³⁵U, respectively, and Pb* is the radiogenic Pb (Faure and Mensing,

2005). The isochron age, t (time), and the error was calculated using IsoplotR software (Vermeesch, 2018). It was considered results that have concordance between 97 and 103% for the calculation age.

2.3 Mass-balance and thermodynamic modeling

The investigation of magmatic differentiation can be conducted by two approaches – the direct and the inverse method (Allègre and Minster, 1978). By the direct method, different models are calculated from a starting point (physical and chemical conditions) and their variables are varied. Then, the obtained results are compared with the data and the best model for the geological problem is selected. The inverse-method approach consists of identifying the model variables fitting a model to the data varying an independent variable of the equation (*e.g.*, Ginibre and Davidson, 2014). Sometimes it is not easy to establish some input variables of the models from the studied intrusion because, for example, part of the body may have already been weathered and volume information is missed. In this case, some of the possible variables are tested. The best fit provides quantitative and qualitative information to build the model of the magmatic differentiation of the studied system. This investigation used the first approach chiefly where different models were employed and variables were varied. Variables such as the starting compositions and fO₂ were assumed or estimated but many others as the initial wall rock temperature, initial wall rock mass and magma recharge mass were varied.

2.3.1 Rayleigh fractionation

In Rayleigh fractionation or fractionation crystallization, the crystallized minerals are separated from the residual melt and the former crystals do not remain in equilibrium with the melt (Ersoy and Helvaci, 2010). This is a closed-system process that is expressed by the Rayleigh Law (5), where C_m^i and C_p^i are the mass fractions of a trace element, i, in the residual magma and in the parental magma, respectively, F is the fraction of melt, \overline{D}_i is the bulk partition coefficient.

$$C_{\rm m}^{\rm i} = C_{\rm p}^{\rm i} F^{(\overline{D}_{\rm i}-1)}$$
(5)

2.3.2 Binary mixing

Mixing consists of putting together two or more different magmas, or endmembers, to form hybrid magmas or a bulk mixing (Langmuir *et al.*, 1978; Albarède, 1995). In this process the mechanic mixing of phases, such minerals, occurs but components of fluid do not preserve previous physical identity after formation of the bulk mixing or hybrid magma (Albarède, 1995). For mixing of two endmembers (α , β), the composition of the bulk mixing, Cⁱ_{mix}, related to specie i is expressed by (6).

$$C^{i}_{mix} = (1 - f_{\beta})C^{i}_{\alpha} + f_{\beta}C^{i}_{\beta}$$
(6)

with
$$f_{\beta} = \frac{M_{\beta}}{M_{0}}$$
 and $f_{\beta} + f_{\alpha} = 1$

Where M_{β} is the mass of the endmember β , M_0 is the total mass and C_{β}^i is the concentration of i in the endmember β . If the equation (6) is rearranged and divided by the equation (7) for element y, then it is obtained the equation (8), which relates the element i with y according to a linear correlation.

$$C_{\rm mix}^{y} - C_{\alpha}^{y} = f_{\beta}(C_{\beta}^{y} - C_{\alpha}^{y})$$
(7)

$$C_{\text{mix}}^{i} - C_{\alpha}^{i} = \frac{(C_{\beta}^{i} - C_{\alpha}^{i})}{(C_{\beta}^{y} - C_{\alpha}^{y})} (C_{\text{mix}}^{y} - C_{\alpha}^{y})$$
(8)

For ratio-ratio plot $\left(\frac{^{87}Sr}{^{86}Sr} \times \frac{^{143}Nd}{^{144}Nd}\right)$ considering the ultrabasic and acid endmembers, the magma mixing expression is given by (9) and (10) forming a hyperbolic array. The $^{87}Sr_{\alpha}$ and $^{87}Sr_{\beta}$ can be replaced by $^{86}Sr_{\alpha}\left(\frac{^{87}Sr_{\alpha}}{^{86}Sr_{\alpha}}\right)$ and $^{86}Sr_{\beta}\left(\frac{^{87}Sr_{\beta}}{^{86}Sr_{\beta}}\right)$, respectively, where $^{86}Sr \sim 0.0987 \times Sr_{total}$ is obtained by means of whole-rock composition.

$$\binom{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{mix}} = \frac{(1 - f_{\beta})^{87}\text{Sr}_{\alpha} + f_{\beta}^{87}\text{Sr}_{\beta}}{(1 - f_{\beta})^{86}\text{Sr}_{\alpha} + f_{\beta}^{86}\text{Sr}_{\beta}}$$
(9)

$$\left(\frac{{}^{143}\text{Nd}}{{}^{144}\text{Nd}} \right)_{\text{mix}} = \frac{(1 - f_{\beta})^{143}\text{Nd}_{\alpha} + f_{\beta}{}^{143}\text{Nd}_{\beta}}{(1 - f_{\beta})^{144}\text{Nd}_{\alpha} + f_{\beta}{}^{144}\text{Nd}_{\beta}}$$
(10)

2.3.3 Assimilation – Fractional crystallization (AFC)

This model encompasses two concomitant processes, the fractional crystallization and continuous crustal assimilation in a magma chamber. The AFC model of DePaolo (1981b) assumes that the system incorporates contaminant melt at constant rate and fractionates crystals in a homogeneous magma. The model follows the equation (11).

$$\frac{C_{\rm m}}{C_{\rm m}^{\rm o}} = F^{-\rm Z} + \left(\frac{r}{r^{-1}}\right) \frac{C_{\rm a}}{z C_{\rm m}^{\rm o}} (1 - F^{-\rm z})$$
(11)

with
$$z = \frac{r + \overline{D_l} - 1}{r - 1}$$
, $F = \frac{M_m}{M_m^0}$ and $r = \frac{\dot{M}_A}{\dot{M}_C}$

where variables are: C_m , C_m^0 , C_a (mass fraction of element i in the magma at time t, in the intrusive magma at initial time t_0 and in the assimilated melt, respectively), $\overline{D_1}$ (bulk partition coefficient of i), \dot{M}_A (rate of wall rock assimilation by the main magma body), \dot{M}_C (rate at which the crystallizing material is separated from the magma), M_m (mass magma) and M_m^0 (initial mass magma). Although the model assumes r and $\overline{D_1}$ as constant variables, DePaolo (1981b) has recognized that both may vary as F decreases in real situations. For higher r values, the model tends to behavior as a magma mixing, but r decreases when an ascent magma reaches a cooler wall rock in the crust (ignoring the effect of change of wall rock composition and pressure on partial meting during the trajectory).

In contrast to the mixing process, where the mass fraction of i tends to be similar to that of crustal melt with increasing mixing, the same pattern is not always achieved in AFC process. For example, C_m may increase in the main magma when $C_a > C_m^0$ and $\overline{D_1} < 1$ and even more with higher r values, whereas C_m may decrease if $\overline{D_1} > 2$ when $0.1 < C_a / C_m^0 < 10$ (DePaolo, 1981b - Fig. 2).

For isotopic ratios, the AFC equation is established according to (12) (DePaolo, 1981b).

$$\frac{\epsilon_{\rm m} - \epsilon_{\rm m}^{\rm 0}}{\epsilon_{\rm a} - \epsilon_{\rm m}^{\rm 0}} = 1 - \left(\frac{c_{\rm m}^{\rm 0}}{c_{\rm m}}\right) F^{-\rm Z}$$
(12)

where ϵ_m and ϵ_m^0 is isotopic ratios of main magma at time t_0 and t, respectively, and ϵ_a is elemental or isotopic ratio of the crustal melt. The effect of AFC on the elemental or

isotope variation (*e.g.*, ⁸⁷Sr/⁸⁶Sr x Sr) in residual melt depends on the set of model variables. When $\dot{M}_A = \dot{M}_C$, Sr content increases relatively more than the ⁸⁷Sr/⁸⁶Sr ratio with $\overline{D_{Sr}} = 0.01$ than with $\overline{D_{Sr}} > 0.25$ (DePaolo, 1981b – Fig. 3b).

Binary mixing (Langmuir et al., 1978; Albarède, 1995) and AFC (DePaolo, 1981b) are mass-balance models. On other hand, MELTS software package (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998), a thermodynamic modeling tool, simulates AFC through equilibrium phase relations. Reiners et al. (1995) have calculated the contaminant mass by the simplified energy-balance equation (13) taking into account 5°C temperature decrease per step. The heat capacities and crystallized mass (equation 13) from the main magma, the compositional evolution of the system were estimated using MELTS software at each temperature decreasing step. The r and the minerals to be crystallized are not constant at this more sophisticate approach. At first moment, the crustal melt precludes part of the fractional crystallization due to the composition change of the basic magma promoted by the assimilation process. Thus, the r value tends to be higher (r>1) in the beginning of the assimilation in the studied conditions. At a later stage, the melt can reach the saturation condition of further minerals and from this point, the r (\leq 1) starts decreasing in their study. The isenthalpic (or enthalpy balance) AFC model employed by Reiners et al. (1995) has shown that the contamination of basalts by crustal rocks at the first stage allows low magma differentiation for major elements because of the low crystallization rate whereas the high assimilation rate may modify the isotope and trace element contents of the magma.

$$M_{a} = \frac{M_{m}C_{p}^{m}\Delta T_{m} + \Delta H_{f}^{c}M_{c}}{C_{p}^{a}\Delta T_{a} + \Delta H_{f}^{a}}$$
(13)

where M_m and M_c are the magma and crystal masses, C_p^m and C_p^a are the heat capacities of magma and crustal contaminant, ΔH_f^c and ΔH_f^a is the latent heats of fusion of the crystals and crustal contaminant which were considered constant for the crystallizing phases.

2.3.4 Magma Chamber Simulator (MCS)

The MCS is a thermodynamic software to model magmatic processes (Bohrson *et al.*, 2014; Bohrson *et al.*, 2020; Heinonen *et al.*, 2020) such AFC, magma recharge (R_nFC , R_nAFC , where n is the number of repetition of the magmatic process) in a resident magma

body. The MCS associates the equilibrium phase relations obtained by MELTS software (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) with species, mass and enthalpy balance equations (Spera and Bohrson, 2001, 2002; Bohrson and Spera 2001, 2003). The software measures the effect of concurrent processes such as crystallization, crustal simulation and magma recharge on the composition and enthalpy of the system. This model considers the system divided into four subsystems: main magma, cumulate, wall rock and magma recharge (Fig. 5). The main magma releases sensible and latent heat toward the wall rock which is heated from its initial temperature through a diabatic borderline. The wall rock starts partially melting if the energy transferred makes the wall rock temperature increases above its solidus temperature. By a semi permeable boundary, the partial melt of wall rock is added in the main magma according to the Emzero variable that stablishes the melt mass fraction accumulated in the wall rock before the anatectic melt to be released into the magma chamber. The Fmzero is an attempt to simulate the partial melt migration from the site of formation after the development of interconnection channels in the wall rock (Bohrson *et al.*, 2020). However, the wall rock is isolated regarding the remaining country rock. In its turn, the basic magma recharge adds enthalpy to the main magma and may aid the wall-rock temperature to increase above its solidus temperature. The minerals from the main magma are fractionated with fluid on the bottom of the magma chamber and keep in thermal equilibrium with the main magma which is thermodynamically in equilibrium with the most recent crystallized minerals. The MCS simulates the magma recharge plus AFC (R_nAFC), assimilation of wall-rock stop blocks plus AFC (S_nAFC) or magma recharge, assimilation of wall-rock stoped blocks plus AFC (R_nS_nAFC) through the same computing process. The software mixes the bulk composition of wall-rock stop blocks or magma recharge with the main magma at defined temperatures and, as a result, fluid and crystals may precipitate. After each assimilation or mixing step, the existent phases in the main magma reach the chemical equilibrium state. The programing or run is terminated when the thermal equilibrium among the subsystems is achieved. The discussion of mass and thermalbalance equations can be accessed mainly in Spera and Bohrson (2001) and Bohrson et al. (2020).

Although the MCS is a more complex modeling tool for magmatic process simulation than those cited above, the MCS was structured based on some simplification of magma chamber representation (Borhson *et al.*, 2020) once some processes are not easily predicted or identified in overall systems. For exemplification, this section mentions two of them. Other simplifications are debated in the chapters below. The model does not



Figure 5: Open-system magmatic processes (AFC, SFC, RAFC) simulated by MCS software. The flux of energy and material among the subsystems (main magma, cumulate, wall rock, wall-rock stoped blocks) are represented. MCS also simulates SAFC, RSAFC and FC (closed-system process) that are not highlighted in the flowchart. Modified from Spera *et al.* (2001), Bohrson *et al.* (2014, 2020).

predict the chemical heterogeneity of the magma chamber (*e.g.*, Ginibre *et al.*, 2002; Kuritani *et al.*, 2005) and the temperature heterogeneity within wall rock (Annen, 2017 and references therein) as observed in some systems. Kuritani *et al.* (2005) have described the mechanism that involves three endmembers in AFC, which the first one is the wall-rock melt, the second one is the interstitial melt of the mush and the last one is the melt of central region of the magma chamber. Part of the initial melt is cooled on the chamber wall and forms the mush zone. The crustal melt percolates the wall-rock fractures and mixes with the melt of the mush zone where there is a continuous fractional crystallization. After this step, the residual melt is transported to the main magma. On the contrary, the MCS model accumulates crystals apart, isolates them chemically from the magma and does not consider mush formation on the wall rock.

The MCS software operates through interface written in Microsoft's Visual Basic programming language (Bohrson *et al.*, 2014; 2020). The input consists of spreadsheet which is filled out and attached to the MCS software (MCS-PhaseEQ - calculator for major and minor elements and phase equilibria). The input variables for major- and minor-element modeling are presented in Table 3. The output comprises the MELTS results released as an Excel workbook which presents the evolution of bulk composition, phase equilibria and abundance of phases of the subsystems as the whole system evolves toward thermal equilibrium. The output also exhibits charts with the calculated data. The thermal data of each phase are released in TBL file format in the respective subsystem file. The Excel workbook output for major and minor elements is attached to the trace-element and isotope calculator. The output consists of a workbook with trace-element and isotope composition of melt, fluid and crystalline phases following the magma evolution result obtained by calculator for major and minor elements.

Table 3: In addition to the starting composition (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, Cr₂O₃, FeO, MnO, MgO, NiO, CoO, CaO, Na₂O, K₂O, P₂O₅, H₂O, CO₂) of the subsystems (main magma, magma recharge, wall rock and wall-rock stoped blocks), the input parameters are listed below. For the further detail of how to vary or select these parameters, consult Bohrson *et al.* (2020). The correspondent symbols are used in the Chapters 3 and 4 as follow.

T ₀ ^{MM}	Initial temperature of the main magma (°C)	M ₀ ^{MM} = 100	Initial mass of the main magma (m.u.)
T_D^{MM}	Temperature decrement (°C / step)	T_{S}^{MM} or M_{S}^{MM}	Hard stop of running according to a minimum temperature (°C) or melt mass (m.u.)
T_0^{WR}	Initial temperature of the wall rock (°C)	M_0^{WR}	Initial mass of the wall rock (m.u.)
T_i^{WR} and T_e^{WR}	Temperature interval (initial, I, and end, e) to find solidus temperature (°C)	$T_{\rm D}^{\rm WR}$	Temperature decrement to find the solidus temperature (°C/step)
T ^{R or S}	Temperature of recharge magma (°C)	M ^{R or S}	Mass of recharge magma (m.u.)
T ^R or S T _{byDeltal}	Recharge trigger mode (temperature when the recharge magma is added): temperature decrement from liquidus temperature of the main magma	T ^{Rpr S} byTemp or T ^{R or S} byTempSerial	Recharge trigger mode: temperature of the main magma or the following (N+1) recharge magma is added when the N recharge magma is completed
Fmzero	Partial melt fraction in the wall rock to be reached before the crustal assimilation in each contamination step	Ρ	Pressure in bar (constant)
Ph	Excluded phases in all subsystems (when it is necessary)	fo ₂	Oxygen fugacity (none, fmq, coh, nno, iw, hm)

Table 4: The input parameters used for trace element and isotope ratio modeling by MCS. The subscript i represents the trace element(s) (*e.g.*, Sr, Ba, Cr, Pb in ppm) and y/Y is the isotope ratio(s) (*e.g.*, ⁸⁷Sr/⁸⁶Sr, ²⁰⁷Pb/²⁰⁴Pb) selected to model. The types and the abundances of crystalline, melt and fluid phases in m.u. are based on the MCS output file attached in the workbook for trace-element and isotope ratio modeling.

$X_i^{MM}, X_{v/Y}^{MM}$	Initial composition of	X ^{WR} , X ^{WR}	Initial composition of					
57	the MM	5,	the WR					
		D ^{phase/(melt or fluid)}	Partition coefficient of					
		or	trace element i					
$X_i^{R \text{ or } S}, X_{v/V}^{R \text{ or } S}$	Initial composition of	$\log D^{\text{phase}/(\text{melt or fluid})} 1$	between phases and					
, y, i	the R or S	$\log D_{i} = \frac{1}{T}$	melt in MM (constant					
			value or in function of					
		in MM	T ⁻¹)*					
D ^{phase/(melt or fluid)}		D ^{phase/(melt or fluid)}						
or	Partition coefficient of	or	Partition coefficient of					
phase/(melt or fluid)_	trace element i	$\log \frac{1}{1}$	trace element i					
log _D	between phases and	$\log D_i = \frac{-}{T}$	between phases and					
<u>+</u> T	melt in WR*		melt in R or S*					
2		in R or S						
in WR								

*The user provides two pairs $(T,D_i^{phase/(melt or fluid)})$ and the software calculates the linear function.

2.4 References

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