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1. INTRODUCTION

Fluid flow is a fundamental process governing the distribution of elements in many geological settings, providing a much more efficient transport mechanism than solid state diffusion. Addition and removal of chemical components and modifications of mineral and bulk composition of rocks are directly linked to metasomatic processes, typically recorded by the dissolution of pre-existing minerals and precipitation of new phases (e.g., Nabelek et al., 2013; Engvik et al., 2018). However, fluid flow often occurs in heterogeneous and anisotropic media, in which case the fluid flow is structurally and/or lithologically controlled resulting in localized metasomatic domains that record the characteristics of fluid-rock interaction over time. Deciphering the spatial and temporal evolution of fluid-mediated rock alteration is crucial to understand complex processes in natural settings. Detailed studies of the zones of metasomatic reactions in terms of reaction textures and spatial distribution hold a wealth of information regarding the conditions at which fluid-rock interaction occurred.

Carbonate rocks and their metamorphic equivalents are typically highly reactive when exposed to externally derived fluids or changing metamorphic conditions (e.g., Bucher-Nurminen, 1981; Müller et al., 2004; Bégué et al., 2020). In particular, crystallizing plutons in contact with carbonate rocks constitute important heat and fluid sources causing metamorphism and skarn formation. Therefore, skarns are useful to obtain information on metasomatic interaction and contact metamorphism conditions. In this paper we use the term skarn for metasomatic rocks made of Ca–Fe–Mg–(Mn)-silicates and carbonates often with sequences of compositional zones and bands, formed by the interaction of a carbonate and a silicate system in mutual contact. If the carbonate part is dominantly made of dolomite, the metasomatic rocks are described as magnesian skarns. This variety of skarn typically contains forsterite, diopside, phlogopite, spinel and/or humites whereas some minerals such as quartz and/or calcite are present in almost all skarns (Meinert et al., 2005).

In general, there is a causal relationship between the sequence of emplacement, crystallization, alteration, and cooling of an intrusion and the corresponding spatial and temporal evolution during prograde and retrograde skarn formation (Brown et al., 1985; Meinert et al., 2005). Detailed knowledge on the mechanisms, rates, and timing of the emplacement of plutonic bodies remains elusive but significantly impacts our understanding of the processes forming the associated metasomatic complexes. For example, several authors proposed that plutons ascend as large diapirs (e.g., Buddington, 1959; Miller & Paterson, 1999) whereas other authors consider this process as slow and inefficient (e.g., Clemens and Mawer, 1992; Petford et al., 2000). Other authors suggest that large igneous magmatic bodies are formed by the incremental supply of magma through dyke- and sill-like structures that can build up a magmatic body over millions of years (e.g., Petford et al., 2000; Coleman et al., 2004). However, the recognition of incrementally assembled plutons recorded in the granitic rocks can be problematic because temperature remains nearly homogeneous for a long time potentially obscuring pristine contacts between individual increments (Bartley et al., 2008). Yet, magmatic pulses with quiet intervals can last for tens of millions of years (i.e., protracted magmatism) and result in overprinted granitic batholiths (e.g., He et al., 2018; Tichomirowa et al., 2019). While the diapir, incremental and protracted models are conceptually plausible, they are characterized by fundamentally different cooling and fluid infiltration histories. Therefore, studying in detail the metasomatic fingerprint of the interaction of magmatic fluids with host rocks offers the potential to reveal the detailed intrusion and infiltration history of a complex plutonic body.

In this contribution, we combine field relations, petrology of metasomatic rocks and LA-ICP-MS U-Pb dating of zircon, titanite and apatite of igneous apophyses of the

Neoproterozoic Caçapava do Sul Granitic Complex (CSGC) to determine the intrusion, deformation, and fluid infiltration history of the complex. The igneous complex intruded into the dolomitic marbles of the Passo Feio Metamorphic Complex (PFMC) on the eastern border of the São Gabriel Terrane, southern Brazil (Fig. 1a). The emplacement of the granitic complex resulted in a metasomatic system recorded by the formation of skarns and hydrothermal veins. The observations and geochronological data are successfully explained by a model of localized and dynamically evolving fluid-rock interaction that provide a full record of the intrusion history of the granitic complex confirming a protracted growth of the magmatic body.

2. GEOLOGICAL BACKGROUND

The Passo Feio Metamorphic Complex (PFMC) and the Caçapava do Sul Granitic Complex (CSGC) are located at the eastern border of the São Gabriel Terrane (SGT), which itself belongs to the Dom Feliciano Belt (DFB) (Figs. 1a-b). The Dom Feliciano Belt represents the southern portion of the Mantiqueira Province, i.e., the Neoproterozoic NE-SW orogenic system that extends from north-eastern Brazil to the south of Uruguay. The São Gabriel Terrane comprises a Neoproterozoic (920-680 Ma) juvenile magmatic arc association developed during the collision of the Kalahari and Rio de La Plata cratons (Fernandes et al., 1992; Hartmann et al., 2000; Saalmann et al., 2011). The terrane is composed of metavolcanic-sedimentary supracrustal sequences that were metamorphosed under amphibolite facies conditions and subsequently intruded by juvenile calc-alkaline magmas, now present as orthogneisses, ophiolites and mafic-ultramafic complexes (Remus et al., 1993; Babinski et al., 1996; Hartmann et al., 2000; Hartmann et al., 2011). Additionally, the São Gabriel Terrane hosts several Neoproterozoic granitic intrusions (e.g., Caçapava do Sul Granitic Complex) and is partially covered by post-collisional volcano-sedimentary sequences.

2.1. Passo Feio Metamorphic Complex

The Passo Feio Metamorphic Complex is in the eastern border of the São Gabriel Terrane and consists of a supracrustal association of metapelite, amphibolite, marble, calc-silicate and metavolcanic rocks that were intruded by the Caçapava do Sul Granitic Complex (Bitencourt, 1983; Hartmann et al., 1990; Remus et al., 2000) in addition to sheeted carbonatite intrusions (Cerva-Alves et al., 2017).

The metamorphic events that formed the Passo Feio Complex have been subject to controversial discussions. While there is a consensus that the complex records at least two metamorphic events displaying an increasing metamorphic grade towards the granitic batholith, contrasting ideas have been proposed regarding the thermal effect of the intrusion on the metamorphic record. Some authors described hornblende-hornfels and pyroxene-hornblende facies rocks surrounding the granite up to a few hundreds of meters from the contact, which were gradually followed by albite-epidote-hornfels and greenschist facies rocks further from the contact based on extensive field mapping of the area (e.g., Silva-Filho & Matsdorf, 1987; Bortolotto, 1988). These authors interpreted the observed distribution of mineral assemblages to be the result of a primary regional metamorphic event ranging from greenschist to amphibolite facies, followed by a second contact metamorphic event associated with the intrusion of the Caçapava do Sul Granitic Complex. In contrast, other authors interpret both metamorphic events as regional, with the first one reaching amphibolite facies (staurolite zone) conditions and the second, synchronous to the intrusion, as a greenschist facies (chlorite zone) with thermal and infiltration effects restricted to the border of some apophyses (Bitencourt, 1983; Hartmann et al., 1990).

Zircon provenance studies in metapelites and schists revealed Archean, Paleoproterozoic and Neoproterozoic populations (3637 to 774 Ma) suggesting complex continental source areas (Remus et al., 2000; Lopes et al., 2015). C, O and Sr isotopic compositions of the dolomitic marbles reveal carbonate deposition between 770 and 730 Ma (Goulart et al., 2013). LA-ICP-MS monazite dating yields a series of ages between 650 and 620 Ma, which were assigned to the first metamorphic event (Remus et al., 2010). The second metamorphic event was then linked to the age of a granodiorite sill sample of the CSGC of 562±8 Ma based on SHRIMP U-Pb zircon dating (Remus et al., 2000).

2.2. Caçapava do Sul Granitic Complex

The Caçapava do Sul Granitic Complex exhibits a wide compositional range with mostly granodiorite, monzogranite, leucogranite, minor diorite, tonalite and quartz-diorite of metaluminous and calc-alkaline affinity (Sartori & Kawashita, 1985; Nardi & Bitencourt, 1989). The granitic batholith to the west of the dolomitic marbles outcrops over an area of c. 233 km² forming a N-S elongated asymmetrical domal structure dipping at high angles in the W and NW parts, at low angles in the E and SE parts, and sub-horizontally in the central parts of the granitic body (Figs. 1b-c) (Sartori & Kawashita, 1985; Nardi & Bitencourt, 1989). Pegmatite, aplitic dykes and quartz veins with pyrite and hematite occur in the eastern border of the body near the dolomitic marbles.

Deformation is heterogeneous throughout the batholith ranging from undeformed portions to highly foliated facies where boundaries between these facies vary from sharp to diffuse. Foliation and banding are common and mostly marked by the preferred orientation of biotite and amphibole, as well as elongate feldspar and quartz grains (Nardi & Bitencourt, 1989). A N-S to NE-SW sub-horizontal mineral grain and aggregate lineation is dominant in the granitic body and the foliation close to the boundary of the batholith is mostly concordant to S_2 foliation of the surrounding metamorphic rocks (Nardi & Bitencourt, 1989). Contrasting emplacement models were proposed: a diapir (Nardi & Bitencourt, 1989), a sheet-like intrusion (Fragoso-César, 1991), a lens-shaped syntectonic batholith (Fernandes et al., 1992) and an intrusion along a fault-bend-fold of a right lateral strike-slip shear zone (Costa et al., 1995).

First attempts to date the Caçapava do Sul Granitic Complex were made through K/Ar and Rb/Sr isochron dating, which resulted in ages ranging from 520 to 640 Ma (Cordani et al., 1974; Sartori & Kawashita, 1985). Two different U-Pb SHRIMP zircon studies were carried out on samples of a monzogranite and a granodiorite revealing a complex distribution of zircon ages indicating significant amounts of lead loss and reversely discordant ages (Leite et al., 1998; Remus et al., 2000). Two magmatic ages were proposed based on SHRIMP zircon U-Pb analyses. The two studies reported two similar concordant ages of 561±6 Ma (MSWD=1.04; n=4; Leite et al., 1998) and 562±8 Ma (MSWD=0.56; n=18; Remus et al., 2000) and one age of 540±11 Ma (MSWD=0.89; n=3; Leite et al., 1998). The younger age of c. 540 Ma was re-interpreted as the result of common Pb loss of older zircons (Remus et al., 2000). Inherited Paleoproterozoic zircon populations with ages ranging from 1.7 to 2.4 Ga were reported in both studies. Large variations in initial $^{87}Sr/^{86}Sr$ and εNd values, lead isotopes and zircon ages also suggest that the CSGC had a complex and heterogeneous crustal source of variable composition and age (Babinski et al., 1996; Remus et al., 2000).

3. SAMPLING AND METHODS

Collection of field data and sampling focused on the Caçapava do Sul marble quarries due to the extensive exposure of marbles, igneous apophyses and metasomatic rocks (skarns and hydrothermal veins) providing the opportunity to sample the best sections for the study of igneous and carbonate rock interaction in the region. Sample collection was made throughout the area aiming at obtaining representative samples of the different igneous components and skarns displaying their various degrees of deformation, spatial relationships, and retrograde alteration. Petrographic analyses were made using a LEICA DM4500 optical microscope and a LEICA S6D Greenough stereo microscope to identify major constituent minerals and textures. Zircon, apatite and titanite grain concentrates were prepared at the Sample Preparation Laboratory at the Geosciences

Institute of UFRGS (IGEO/UFRGS) using conventional jaw crusher, milling, manual panning, magnetic-Frantz isodynamic separator and heavy liquids separation. The grains were handpicked under a binocular microscope and mounted on epoxy disks. U-Pb laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of zircon, apatite and titanite samples were performed at the Isotopic Geochemistry Laboratory, Federal University of Ouro Preto (IGL-UFOP). Back-scattered electron (BSE) and cathodoluminescence (CL) images were obtained with a JEOL JSM-6610LV and a JEOL 6510 scanning electron microscopes at IGEO-UFRGS and DEGEO-UFOP, respectively, to identify internal structures of the crystals. The LA-ICP-MS analyses were performed using a ThermoScientific Element 2 sector field (SF) ICP-MS coupled to a CETAC LSX-213 G2+ laser system. Spot sizes were set at 30 μm for zircon and 50 μm for titanite and apatite. Zircon analyses calibration included GJ-1 (Jackson et al., 2004) with the additional Plešovice (Sláma et al., 2008) and Blue Berry (Santos et al., 2017) zircon standards. For titanite and apatite reference materials, BLR-1 (Aleinikoff et al., 2007) and KHAN (Kinny et al., 1994) were used for the titanite while 401 (Thompson et al., 2016) and Madagascar (Thomson et al., 2012) were used for the apatite. Glitter Data Reduction Software for laser ablation was used to reduce data (Van Achterberg et al., 2001). Calculated ages and concordia diagrams were done using Isoplot 3.0 (Ludwig, 2003) and errors are reported at the 2σ level. The calculated titanite and apatite ages are the lower intercept of anchored regressions through the $^{207}Pb/^{206}Pb$ ratio of the crustal lead at the time of formation of the titanite and apatite (i.e., Pbc), as defined by Stacey and Kramers (1975) on the Tera-Wasserburg diagram. The anchoring ratios are based on the samples intercept age and the zircon ages. T-XCO_2 and XCO_2-μSiO_2 phase diagrams were calculated using PerpleX (Connolly, 1990) using the dataset from Berman (1996) and equation of state for fluids from Holland and Powell (2011). Abbreviations for the mineral names and their end-members described in the text and figures are after Whitney and Evans (2010).

4. GENERAL FIELD RELATIONSHIPS

Dolomitic marbles are present in the eastern portion of the metamorphic complex and occur as lenticular bodies that are extensively intruded by tabular felsic and mafic apophyses of variable thickness and composition (Figs. 2a-d). They occur to the east of the main granitic body of the CSGC (i.e., the granitic batholith; Figs. 1b-c) with sharp and eastward dipping contact at low to medium angles (~10-30°). In this paper, we refer to the bedding of the marbles as S_0 and the metamorphic foliation developed during the first metamorphic event (regional amphibolite facies conditions) prior to the first magmatic intrusions as S_1. Bedding (S_0) is generally difficult to decipher except where there is compositional change characterized by fine to medium grained metamorphic layers with talc and tremolite resulting in gray tones (Fig. 2f). The silicate content of the dolomitic marbles varies from 2% in massive white marbles up to 15% in banded gray layers. S_1 foliation is well developed and defined by elongated crystals of dolomite, dominantly parallel to bedding. The marbles and some of the apophyses (mainly mafic ones) form overturned to recumbent isoclinal folds with N-S to NE-SW fold axis that plunges at low angles mostly to the S-SW (Figs. 2a-e). The axial surfaces define the S_2 foliation. The average axial surface dips 20° to the east, locally varying to sub-horizontal or rarely dipping westward at low angles (<15°). Ductile deformation prevails towards the contact with the granitic batholith (i.e., Dagoberto Barcelos quarry area (DB); Fig. 1b). Marbles with a platy aspect caused by the foliation and highlighted by an intercalation of low and high strain areas (Fig. 2f) prevail in the eastern portion of the metamorphic complex (i.e., Inducal quarry area (IN); Fig. 1b). Low strain areas are characterized by a grain size of a few millimetres (~2 mm) and granular aspect with nearly equidimensional grains. In contrast, the high strain portions exhibit a range of grain sizes including 1-2 mm-sized porphyroclasts within a fine-grained matrix, elongate crystal shapes seen for larger grains and a closely spaced foliation (Fig. 2f).

Tabular felsic and mafic intrusions within the dolomitic marbles are well exposed in the quarries. A group of mafic and felsic apophyses with small to moderate thickness (~0.1 to 1 m) intruded parallel to the S_1 foliation of the marbles and are folded during the deformation event that produced the S_2 foliation (Figs. 2a-d). For simplification, this group of thin and folded mafic-felsic apophyses are identified as A1. A1 mafic apophyses form tabular bodies predominantly continuous for tens to hundreds of meters and concordant to the S_1 foliation. A1 mafic apophysis-marble contacts vary from sharp to diffuse. A1 apophyses are often strongly foliated and marked by the preferred orientation of mafic minerals. The observed foliation is parallel to sill orientation and to S_1 foliation of the country rocks. There are no clear cross-cutting relationships between the A1 mafic and felsic apophyses; instead, if they occur in the same outcrop, they are seen to form one intrusive body with interlayered mafic and felsic bands with parallel boundaries (Figs. 2b-d; 6a). This suggests that these composite mafic-felsic sills formed contemporaneously from A1 mafic and felsic magmas.

Thicker tabular felsic apophyses (> 2 m) intruded the marbles parallel or sub-parallel to the S_2 foliation and are referred to in the following as A2. Given that the orientation of A2 apophyses is parallel to the S_2 axial plane foliation and that A2 apophyses host mafic enclaves (Fig. 6b), likely from A1 apophyses, we consider A2 younger than A1. However, in some cases, distinguishing A2 and A1 felsic apophyses is difficult. Main criteria used for distinguishing A1 and A2 felsic apophyses are thickness, grain-size, and emplacement-host geometry. A1 felsic apophyses are thin (20-100 cm), have fine to medium grain size and are commonly folded whereas A2 apophyses are thicker (~ 2 to >10 m), have medium to coarse grain size and emplaced parallel to the S_2 axial plane foliation (Section 4.4.2). Contacts of A2 apophyses with the marbles are often sharp and unreacted, although diopside and forsterite skarns are developed in the dolomites at many of these contacts (Figs. 3a-b). A2 apophyses are mainly represented by granodiorite, monzogranite and syenogranite intrusions, which correspond to the main facies of the Caçapava do Sul Granitic Complex described in previous studies (e.g., Nardi & Bitencourt, 1989). Late pegmatite bodies and leucogranites are associated with the A2 intrusions and occur as small portions within sills (Figs. 3b and 6b) or as irregular bodies predominantly cutting A1 and A2 mafic and felsic apophyses (Fig. 6d).

The marbles were locally replaced by skarns that are found at the contacts or a few meters away from A1 and A2 apophyses (Figs. 2d,g; 3a-d; 4a-c). Skarns at the lithological contacts of A1 apophyses are asymmetric relative to the lithological boundaries, i.e., skarn is not always developed at each lithological interface (Fig. 3c). Even along the same apophysis-country rock interface, the skarn is discontinuous (Fig. 3a). There is no preferred occurrence of skarns in the structurally upper or lower borders of the apophyses. Skarn bodies are variable in thickness (5 – 100 cm) and texture (Figs. 3c-d). Thicknesses are generally higher close to the apophysis-country rock contact and thin away from the contact. No spatial relation between the contact type and thickness of the skarn was identified. Nevertheless, skarns are more frequent at fold hinge zones or terminations of the A1 mafic apophyses (Figs. 2d and 3c). Bodies of skarn commonly form parallel to the pre-existing S_1 foliation (Fig. 3a). However, the skarns locally crosscut the S_1 regional metamorphic foliation (Figs. 2g and 3a). Skarns are also seen to “follow” S_2 foliations and form sigmoidal extension veins (Fig. 2g).

Skarns are divided into diopside and forsterite skarns. Diopside skarns consist of coarse diopside grains with variable amounts of sulphides and tremolite + calcite whereas forsterite skarns consist of two zones defined by the silicate present, i.e., forsterite and phlogopite zones. The phlogopite zone, however, is difficult to recognize in the field due to its macroscopic similarity to the dolomitic marbles. The skarns are frequently associated with each other resulting in zoned skarns where the diopside zone typically occurs in the center, bordered, or partly replaced by the forsterite and phlogopite zones (Figs. 3c-d; 4b-c). The two skarn types occur either separately or combined. If combined, then the di-skarn is at the centre and the fo-skarn at the interface to the country rock (Figs. 3d and 4b-c). There is no systematic spatial difference in association with A1 and A2 for the two skarn types. Both skarn types are seen to forming extensional features with diopside skarn forming pinch-and-swell and boudin structures with clear shear fractures (e.g., Fig. 4a) while forsterite skarn show a lack of fractures but gentle pinch and swell structures (Figs. 3b; 4a). Less commonly and limited to the northernmost quarry (CL area in Fig. 1b), the carbonates host calcite-chlorite-sulphide veins and breccias that cut S_1 and S_2 foliation and are generally found a few to tens of meters from NW-SE subvertical faults (Figs. 5a-c).

5. PETROGRAPHY AND MICROSTRUCTURES

In this section, we describe the petrographic characteristics of igneous apophyses and skarns. Petrographic and geochemical characterization of the main facies of the granitic batholith can be found in previous studies (Sartori & Kawashita, 1985; Nardi & Bitencourt, 1989). Petrography and geochemistry of the dolomitic marbles were presented and discussed in Goulart et al. (2013).

5.1. A1 mafic and felsic apophyses

Even though the mafic intrusions show similar aspects in the field, mineral assemblages and microstructures reveal heterogeneity among A1 mafic apophyses. Typical mineral assemblages consist of amphibole + biotite + plagioclase ± K-feldspar ± quartz (Figs. 7a-d and 8d-f). Amphibole + biotite + plagioclase are present in all samples in variable proportions (Figs. 7a-d) whereas K-feldspar and quartz occur in some of the samples (Figs. 7a, 7c and 8d). Felsic minerals (quartz, plagioclase and K-feldspar) occur mostly in the groundmass. Amphiboles vary from subhedral short hornblende grains (Figs. 7c and 8d) to subhedral short to elongate actinolite (Figs. 7c and 8e-f) and less commonly subhedral to euhedral tremolite. In general, biotite occurs as discontinuous lenticular and often anastomosing aggregates (Figs. 7a-d and 8e-f). Biotite also occurs as inclusions in coarse grained and equidimensional hornblende crystals that resembles phenocrysts. The foliation in these rocks is well defined by the preferred orientation of the actinolite and biotite (Figs. 7a-d). Biotite and amphibole occur as phenocrysts and in the groundmass. Some samples also show a subtle crenulation highlighted by shear bands defined by the biotite (Fig. 7b). Local chloritization of biotite occurs near fractures or micro shear zones (Fig. 7a). Titanite and apatite are common accessories. Titanite occur mostly within biotite aggregates and less commonly included in hornblende (Figs. 8a-d) whereas apatite is frequently found in the grain boundaries of actinolite and generally with the same preferred orientation as that of the amphiboles (Figs. 8b-c). Disseminated pyrite and chalcopyrite were identified in all A1 mafic apophyses in variable amounts; higher contents were observed in samples located up to tens of meters away from sub-vertical NW-SE trending faults that cut the A1 mafic apophyses in the northernmost quarry (CL area in Fig. 1b). In a few places, molybdenite was found disseminated in the A1 mafic apophyses.

A1 felsic apophyses are less common than A1 mafic apophyses and A2 felsic apophyses. In general, the A1 felsic apophyses comprise equigranular fine to medium grained (0.05 – 0.2 mm) rocks composed of K-feldspar, quartz, plagioclase, and biotite (Figs. 9a-b). Disseminated apatite and pyrite are common (Fig. 9b). Biotite occurs mainly along K-feldspar and quartz grain boundaries and its preferred orientation characterizes a subtle foliation in the A1 felsic apophyses (Figs. 9a-b).

5.2. A2 felsic apophyses

The A2 felsic apophyses comprise mostly granodiorite, monzogranite and less commonly syenogranite and pegmatite. Biotite and hornblende are the main mafic minerals and biotite-hornblende granodiorites represent the most common type of A2 felsic apophyses (Figs. 9c-d). Quartz, K-feldspar, and plagioclase occur in various proportions amongst different apophyses. Foliation in these rocks is characterized by the preferred orientation of biotite, amphibole, and K-feldspar phenocrysts (Fig. 6c). The grain size and the amount and proportion of biotite and amphibole is variable from one sill to another but are nearly homogeneous within the same sill. K-feldspar phenocrysts are common and often occur elongate or with lobate boundaries (Fig. 9d). Quartz grains generally show undulose extinction and occur as recrystallized, 0.1 - 0.5 mm-sized grains with sutured boundaries (Fig. 9c). Allanite and titanite occur as accessory phases in granodiorites and monzogranites, as inclusions in K-feldspar phenocrysts or in contact with biotite and calcic amphiboles. Euhedral coarse garnet, titanite and biotite and disseminated pyrite, molybdenite and chalcopyrite are common in syenogranites and pegmatite bodies. Prismatic elongated zircons to small, rounded zircons are present. Biotite chloritization is common and mainly observed in the samples with a brownish-red colour in the field. This alteration is more frequently found near fault zones, especially in the central and northern quarries of the marble district (CL, FD and AT areas; Fig. 1b). Chloritites formed after intense hydrothermal alteration at c. 300°C of A2 felsic apophyses is found in the northernmost quarry (CL area) (Reis et al., 2017; Hoerlle et al., 2023).

5.3. Skarns

5.3.1. Diopside skarns

The diopside skarns consist of white to green aggregates of diopside (± calcite ± tremolite ± Fe-Cu-Mo sulphides) typically forming irregularly shaped boudin and pinch-and-swell structures (Figs. 4a-c) within the marbles or locally bordering only A1 mafic apophyses (Figs. 3c-d). When bordering the A1 mafic apophyses they show variable thicknesses on each border of the apophysis (Figs. 3c-d) and are often present at one border of the sill only. The coarse grained diopsides are commonly replaced by medium to fine grained tremolite and serpentine. Diopside skarns were not observed bordering A2 felsic apophyses. The diopside skarns occur mostly parallel to the metamorphic foliation (S_1), are rarely folded with the marble layers, and often replace marble mylonitic layers (Fig. 4a). The thickness of diopside skarns varies from a few centimetres reaching more than 50 cm, with the majority ranging from 3 to 15 cm. They are commonly bordered by forsterite skarns (Figs. 3a; 4b-c). The coarse diopside grains or aggregates that vary from millimetre to centimetre sized crystals. They host pyrite, pyrrhotite, molybdenite, micrometre sized calcite and tremolite and rarely phlogopite inclusions. Where fracturing is more intense, diopside grains tend to be divided into sub-grains and partially replaced by millimetre sized tremolite and calcite, which also crystallize along the grain boundaries and fractures. Modal abundances of diopside, tremolite, and calcite in diopside skarns vary significantly from 70-100% diopside, 0-17% tremolite and 0-13% calcite. Diopside grain boundaries are sharp when in contact with coarse grained forsterite-zone (Figs. 10a-b) or irregular/corroded when bordered by fine grained trails of forsterite (Figs. 10a,c). Locally, diopside grains are partially to fully replaced by antigorite.

5.3.2. Forsterite skarns

The forsterite skarns comprise the most common and widespread skarn type that often border diopside skarns (Figs. 3a,c,d and 4b-c), A1 and A2 apophyses (Fig. 3b) or occur as isolated lenses (Figs. 3b-c and 4a). Even though they are mostly oriented parallel to the metamorphic foliation, forsterite skarns often crosscut the foliation A1 or occur as thicker aggregates near felsic apophyses terminations (Fig. 3b). This skarn type comprises a forsterite + calcite zone (forsterite zone) bordered by phlogopite + dolomite + calcite zone (phlogopite zone).

The forsterite zone consists of µm to mm rounded fosterite clusters in a calcite matrix forming planar arrays. Coarser grained forsterite clusters are mostly located in low-strain zones whereas thin arrays with micrometric forsterite trails are in higher strain zones (Fig. 4c). Rounded olivine grains occur in an irregularly shaped calcite matrix (Fig. 10a). In general, the modal distribution between forsterite and calcite is 65% to 35%, respectively. Anhedral pyrite often occurs disseminated in the calcite matrix of the forsterite zone. The calcite matrix shows variable amounts of dolomite exsolution. Commonly, small lamellae of phlogopite occurs within the forsterite zone. Rarely, the forsterite zone contains green spinel and chlorite aggregates. Most locations have portions of partially preserved to fully replaced forsterite. Macroscopic black rounded grains are preserved olivine whereas green to light green rounded grains are partially or fully replaced by serpentine. Serpentinization is more intense near brittle structures and mainly fault zones. The degree of serpentinization is generally homogeneous within the same sample but variable in different samples.

At the outer portion of the forsterite skarns, the phlogopite zone is composed of fine-grained light-brown to colourless phlogopite in a white dolomite + calcite matrix. This zone is always present between the forsterite zone and the dolomitic marble. Its thickness varies roughly proportionally to the width of the respective forsterite zone. The transition from the forsterite zone to the phlogopite zone is irregular and the main changes are the variation from a calcite to a mainly dolomitic matrix, the absence of forsterite and the increase in the abundance and grain size of phlogopite (Fig. 10a). The carbonates in the phlogopite zone form a granoblastic texture with elongate subhedral to euhedral dolomites whereas irregular-shaped calcite occurs along dolomite or phlogopite grain boundaries (Fig. 10d). The dolomite and phlogopite are generally oriented parallel with the same orientation of the forsterite arrays and boundaries of the diopside skarns. The modal abundances of phlogopite vary from 5 to 15%, 5-10% of calcite and 80-90% of dolomite. The phlogopite zone differs from the host dolomitic marbles mainly in silicate content (tremolite and talc in host rocks versus phlogopite in skarns) and microstructures (sutured dolomite grains in host rocks versus elongate polygonal dolomite in the phlogopite zone). Phlogopite is a typical mica occurring in magnesian skarns worldwide (Meinert et al., 2005; Sieber et al., 2020). Phlogopite is partially to fully replaced by antigorite in retrograded samples.

5.4. Hydrothermal veins and breccias

Distinct fracture filling veins, stockworks and breccias are present within the area. They are mostly found in the north of the marble quarry district (CL area; Fig. 1b) where they occur a few to tens of meters away from subvertical NW trending fault zones and areas of brittle deformation, mainly crosscutting the metamorphic foliation and skarns (Fig. 5a). They are not folded and commonly form stockworks (Figs. 5b-c). They consist of centimetre sized veins with coarse euhedral calcite crystals and massive chalcopyrite and pyrite aggregates cemented by chlorite and calcite (Figs. 5b-c). Locally, veins can reach more than 30 cm of thickness and coarser calcite crystals exceed 5 cm. Symmetrical rims around the veins are characterized by high abundance of serpentine within a few centimetres into the host marble (Figs. 5a-d). Breccias are composed of marble fragments and coarse subhedral calcites cemented by massive chlorite, pyrite, and chalcopyrite (Fig. 5d).

6. LA-ICP-MS U-Pb GEOCHRONOLOGY

6.1. Zircon U-Pb ages

6.1.1. A1 mafic apophyses

Zircons from a foliated fine grained mafic apophysis (DB area; DB-G1Z sample; location shown in Fig. 3b) have an average length of c. 120 μm and a maximum of 170 μm. The aspect ratio varies from 2:1 to 3:1 and the zircon crystals are dominantly sub-rounded (Fig. 11d). Grains are either unzoned or irregularly sector zoned. Twenty discordant grains combined with five concordant zircons formed a discordia line that yielded an upper intercept $^{207}Pb/^{206}Pb$ age of 1787±14 Ma (MSWD = 2.4; Fig. 11b; Table S1). Three discordant analyses combined with three concordant grains formed another discordia line that resulted in an upper intercept $^{207}Pb/^{206}Pb$ age of 2190±20 Ma (MSWD = 0.64; Fig. 11b; Table S1). Both Paleoproterozoic ages are interpreted as inherited ages. Previous geochronology studies in the Caçapava do Sul Granitic Complex indicated inherited zircon grains with ages ranging from 2.7 Ga to 0.7 Ga (Leite et al., 1998; Remus et al., 2000).

6.1.2. A2 felsic apophysis

A total of 28 zircons were separated and analysed from a gray medium grained biotite-hornblende granodiorite (DB area; DB-G2Z sample; location shown Fig. 3b). The grains are mostly prismatic and have an average length of c. 215 μm and aspect ratio of 4:1 reaching up to a maximum of 340 μm and 6:1, respectively (igneous zircons of Fig. 11c). Twenty-two analyses on prismatic zircon grains with concentric or patchy CL zoning including cores and rims (Fig. 11c) yielded a concordia $^{206}Pb/^{238}U$ age of 578.0±4.7 Ma (MSWD = 4.5; N = 22; Fig. 11a; Table S2) interpreted as the magmatic age of the sill. Two spots on prismatic grains with concentric zoning are highly discordant (10 and 62% conc.); and four smaller subrounded grains (Fig. 11c) yield inherited concordant ages of 611±18; 1231±16, 1733±45 and 2045±25 Ma.

6.2. Apatite and titanite ages

6.2.1. Mafic apophysis (A1)

Titanites were separated from a mafic apophysis sample (AT area; AT-Z-01 sample) in a quarry-scale fold hinge area. The rock is composed of actinolite (27%), biotite (23%), K-feldspar (24%) plagioclase (21%) and quartz (3%) with titanite, apatite, pyrite as common accessory phases and very fine-grained zircon as traces. Titanite occurs included in biotite and amphiboles or along their grain boundaries (Figs. 7c; 8a-b). Size of analysed grains ranges from 100 to 200 μm. Biotite and apatite are commonly included in the titanite, which also host allanite, rutile, and quartz inclusions (Fig. 8d). BSE imaging shows simple or patchy zoning in the titanites. Twenty grains were analysed aiming to cover different zones. A Tera-Wasserburg plot of titanite analytical results define a discordant array with a lower intercept on the concordia at 556.1±2.9 Ma (Pbc S/K = 0.869; MSWD = 1.2; N = 20; Fig. 12a; Table S3).

Apatite samples were separated from two A1 mafic apophyses (AT area; AT-Z-02; AT-Z-03) that are mainly composed of phlogopite (40%), actinolite (40%), plagioclase (20%) and apatite as main accessory phase. The analysed apatite grains are mainly prismatic, colourless, and have an average size of c. 150 μm reaching up to a maximum of 270 μm. They occur mainly in the grain boundaries with the same preferred orientation of the actinolite and phlogopite, but also included in the amphibole and plagioclase (Figs. 8e-f). BSE and CL imaging revealed the absence of zoning and inclusions in the apatite crystals. The Tera-Wasserburg plots of apatite analytical results define discordant arrays with lower intercepts on the concordia at 557.8±3.4 Ma (Pbc S/K = 0.873; MSWD = 0.97; N = 20; Fig. 12b; Table S4) and 557.0±4.9 Ma (Pbc S/K = 0.873; MSWD = 0.51; N = 18; Fig. 12c; Table S5).

7. DISCUSSION

7.1. Igneous emplacement sequence, geochronology, and related tectonics

Crosscutting relationships and structural patterns of the igneous apophyses suggest that A1 mafic and felsic apophyses intruded the marbles and were subsequently deformed (Figs. 2a-d; 14a-b). A different set of unfolded thicker felsic sills (> 2 m; A2) emplaced in the axial planes of A1 apophyses indicate that larger volumes of felsic magmatism intruded the marbles in a second event after the A1 intrusions (Fig. 14b). The orientation of the A2 apophyses and the preferred orientation of the minerals within these intrusions are parallel to the S_2 metamorphic foliation and the axial surfaces of the A1 folded intrusions. Many A2 apophyses show features that indicate folding during the intrusion (e.g., Fig. 6b) hence A2 was synkinematic to the S_2 forming event, which was previously proposed by Nardi & Bitencourt (1989) who describe an igneous foliation throughout the granitic batholith parallel to the S_2 foliation of the PFMC and suggests that most of the batholith was syntectonic. A1 mafic apophyses were not described in the inner portions of the granitic batholith which suggests that most of the body was assembled by the A2 felsic apophyses and subsequent intrusions and that A1-related magmatism had restricted volume. Field aspects and mineral assemblages of A1 mafic apophyses suggest that these rocks were metamorphosed after a mafic protolith. However, their composition and structural response are distinct from typical metabasalts. High amounts of biotite and amphibole (up to 80%) and the co-existence of hydrous Mg-rich minerals with K-feldspar and quartz are uncommon in metabasalts. A recent study shows that A1 mafic apophyses were initially mafic rocks (i.e., basalts) that were metamorphosed and altered during the intrusion of A2 felsic intrusions of the Caçapava do Sul Granitic Complex (Hoerlle et al., 2022).

Attempts to obtain a magmatic age for the A1 mafic apophyses resulted in inherited ages only (sample DB-G1Z; Figs. 3c and 11b). The composite character of the mafic-felsic intrusive bodies indicates a contemporaneous intrusion of the A1 felsic and mafic apophyses (Figs. 6a). A similar bimodal character with contemporaneous mafic and felsic volcanism between 600 and 580 Ma has been described in the region associated with an extensional regime during the early stages of the development of the Camaquã Basin (Wildner et al., 1999; Janikian et al., 2012; Oliveira et al., 2014). Therefore, we interpret the A1 mafic-felsic intrusions as correlated to this extensional magmatism. Bimodal magmatism typically occurs in extensional environments in various tectonic settings (e.g., Hochstaedter et al., 1990; Jolly et al., 2008). We interpret the A1 intrusions in an overall extensional setting between 600 and 580 Ma hence mafic apophyses are likely limited to this time span. The age of 578±4.7 Ma was obtained for a A2 felsic apophysis, which is interpreted to be formed during a compressive regime. Therefore, the transition from an extensional related mafic-felsic magmatism (A1) to a compressional regime with felsic-dominated magmatism (A2) occurred most likely between 590 and 580 Ma.

The complexity of deciphering the magmatic source of the Caçapava do Sul Granitic Complex was highlighted in previous studies (Nardi & Bitencourt 1989; Babinski et al., 1996; Remus et al., 2000; Hoerlle et al., 2022). To the same end, the variable inherited zircon populations identified in the A2 felsic apophysis, A1 mafic apophysis and in previous studies (Leite et al. 1998; Remus et al., 2000) equally point towards a heterogeneous magmatic source. Inherited zircon grains of c. 600 Ma were identified in the A2 felsic apophysis and in granodiorites from previous studies (Remus et al., 2000), which suggests that igneous rocks from the preceding magmatic event were also sources for the A2 magma.

The consistent ages obtained from titanite and apatite from three A1 mafic apophyses samples suggest that the U-Pb closure or resetting of these minerals occurred at c. 557 Ma. Titanite and apatite have different Pb closure temperatures typically of 500-650°C (e.g., Cherniak, 1993) and 375-600°C (e.g., Cochrane et al., 2014) respectively. Since both minerals record the same age within the error, it is likely that the isotopic closure occurred below 500°C. Additionally, apatite is considered highly susceptible to metasomatic processes at variable pressures and temperatures (e.g., Spear & Pyle, 2002; Harlov, 2015; Kirkland et al., 2018). Field relationships show that the A1 mafic apophyses crystallized before the S_2 forming event and the intrusion of A2 felsic apophyses (A2 is synkinematic to S_2). Therefore, the age recorded by titanite and apatite cannot represent the age of the crystallization of the A1 mafic apophyses. If we consider that A1 magmatism occurred at some point between 600 and 580 Ma and A2 at c. 578 Ma, another source of heat and fluids is needed at c. 557 Ma to reset the titanite and apatite. Two possible explanations are presented for the age recorded in titanite and apatite. We interpret that previously dated intrusions of c. 560 Ma (Leite et al., 1998; Remus et al., 2000) represent a different magmatic pulse and heat from this episode resets the titanite and apatite in the A1 mafic apophyses. In this case, protracted magmatism was responsible for the assembly of the granitic complex with a finite number of discrete pulses with cooling between pulses. Protracted assembly of plutons is recognized worldwide and commonly results in overprinted granites with heterogeneous textures and chemistry (e.g., He et al., 2018; Tichomirowa et al., 2019). The last pulse that heated the wallrocks and caused fluid infiltration led to resetting of the titanite and apatite dates in the A1 mafic apophyses at c. 557 Ma.

Alternatively, the A2 apophysis and previously dated intrusions of Leite et al. (1998) and Remus et al. (2000) represent ages of the incremental intrusion of felsic magmas from c. 578 to 562 Ma resulting in the assembly of the CSGC. The heat from continuous intrusions maintains elevated temperatures (>500°) in the system, results in metamorphism of the A1 mafic apophyses and opens the isotopic system for titanite and apatite. The age of 557 Ma is recorded in apatite and titanite when magmatism ceased and temperature dropped below c. 500°C, defining the late magmatic stage of the system. However, if this alternative hypothesis is correct, temperatures within the batholith and inner aureole were maintained continuously at >500°C for c. 20 My. This implies that the thermal aureole surrounding the batholith would be very wide. The discussion of the width of the thermal aureole is out of the scope of this paper and future studies of the aureole may provide useful insights into the hypothesis of a continuously assembled batholith over 20 My. Nevertheless, both alternatives suggest that the CSGC was assembled from several intrusions from c. 578 to 557 Ma and that apatite and titanite record the age of late magmatism in the area (Fig. 14a-c).

7.2. Multistage fluid influx and associated metasomatic rocks reveals details of intrusion history of the syntectonic Caçapava do Sul Granitic Complex

Magnesian skarns commonly have similar assemblages of those formed during isochemical metamorphism of impure dolomites. Here, evidence indicate that the skarn assemblages were formed from the infiltration of magmatic fluids in opposition to isochemical metamorphism for the following reasons: (i) spatial coincidence of skarn bodies and igneous apophyses (Figs. 2d and 3a-d); (ii) the skarns locally crosscut the S_0 bedding and the S_1 regional metamorphic foliation (Figs. 2g and 3a); (iii) minor occurrence and finer-grained silicate phases (tremolite and talc) in the unreacted dolomite parts versus coarse-grained diopside and forsterite in the skarns; and (iv) presence of molybdenite, pyrite and pyrrhotite associated with the skarns (Figs. 10a-b). The presence of the sulphides in the skarns (Fig. 10a) indicates the presence of Fe, Mo, Cu and other metals dissolved in the magmatic fluid in addition to silica. We note, however, that previous studies in magnesian skarns indicate that the main skarn minerals such as forsterite, diopside, or periclase do not contain significant amounts of iron; hence, the iron in solution tends to form oxides or sulphides rather than andradite or hedenbergite, for example (Hall et al., 1988).

The two main groups of metasomatic rocks (skarns and hydrothermal veins and breccias) hosted by the marbles of the Passo Feio Metamorphic Complex are associated with two main stages of the crystallization history of the Caçapava do Sul Granitic Complex. The di- and fo-skarns are considered to be formed during the emplacement of A2 felsic intrusions because (i) they are seen both along A2 and A1 contacts (Figs. 3a-d and 14b; A2 is younger than A1, see section 7.1); (ii) they show deformation features following S_2 formation (e.g., sigmoidal extension veins; Fig. 2g) and (iii) they are common at S_2 fold hinges (Fig. 3d and 14b; A2 is syntectonic to the S_2 forming event). In addition, field relationships indicate that formation of the forsterite skarns is related to the emplacement of the pegmatitic portions of the A2 felsic apophyses, and the spatial patterns of pegmatites and forsterite skarns highlight the source and pathways of the fluids (Fig. 3b and b'). Hence, we consider that the age of the forsterite skarns can be directly associated with the age of the adjacent A2 felsic apophysis of 578±4.7 Ma (sample DB-G2Z; Fig. 3b).

The second group of metasomatic rocks, the calcite-chlorite-sulphide veins and breccias (Fig. 5a-d), is associated with cooling and uplift of the granitic complex at the end of the magmatic activity because of the lower temperature of the vein assemblages (chlorite, antigorite) and the abundant Fe-Cu sulphide content, previously associated with the late hydrothermal activity of the CSGC (Remus et al., 2000; Reis et al., 2017). The age of the lower-T hydrothermal veins and breccias formation is associated with the cooling event recorded in titanite and apatite at c. 557 Ma. The genesis and evolution of each stage is discussed in the sections below.

7.2.1. Diopside and forsterite skarn formation associated with A2 felsic intrusions

The diopside and forsterite skarns occur as either isolated bodies (e.g., Figs. 3b and 4a) or, more commonly, zoned di-fo-skarns (e.g., Figs. 3a; 3c-d; 4b-c). We note that when isolated, the size of the skarn is much smaller compared to the zoned di-fo-skarns. Isolated forsterite skarns occur typically as mm- to cm-sized arrays and are more common than isolated diopside skarns. Given that diopside and forsterite are (i) frequently combined; (ii) occur along similar interfaces, both spatially close to A2 apophyses; (iii) show similar deformation patterns and (iv) both are stable at high temperatures (e.g., 600 °C), we consider that they most likely formed during the same event. Considering that, we interpret that the variations in fluid composition (e.g., $aSiO_2$; XCO_2) or fluid flux are the controlling factors governing the formation of different assemblages.

In the diopside skarns, tremolite is only found as a minor phase along diopside fractures and texturally interpreted to be a product of retrogression. The retrogressive tremolite is different from the tremolite grains found in the unaltered impure dolomitic marbles formed during the prior regional metamorphism (e.g., Goulart et al., 2013). Hence, we interpret the prograde formation of diopside to proceed via a reaction of dolomite with SiO_2-bearing fluids released from the cooling apophyses:

$$2SiO_{2\,(aq)} + Dol = Di + 2CO_2 \quad (R1)$$

This reaction will be a function of pressure, temperature, $X(CO_2)$ and $a(SiO_2)$ conditions. Previous studies suggest pressures between 0.45 and 0.5 GPa for the A2 emplacement conditions, based on the presence of igneous muscovite in the felsic apophyses by Nardi & Bitencourt (1989) and amphibole-plagioclase geobarometry calculations (Hoerlle et al., 2023). There are no direct constraints yet available on temperature of formation of the diopside skarn. However, studies of calcite inclusions in forsterite from forsterite skarns in the same area reported temperatures between 590 and 630 °C for the crystallization of forsterite and calcite (Hoerlle et al., 2019; 2023). In addition, previous fluid inclusion studies indicate that, in general, the temperature of skarn formation varies from 100 °C to 650 °C (Bodnar et al., 2013). Assuming that di-skarns did not form at lower temperature than fo-skarns, we argue that the diopside formed at a minimum temperature of 590°C. At this condition, the diopside could form either at high values for $X(CO_2)$ >0.8 (Fig. 13a; arrow 1) or at low values for $X(CO_2)$ < 0.2 and low values for $a(SiO_2)$ from ~0.2 to ~0.5 (Fig. 13a; arrow 3).

Forsterite and calcite likely resulted from the reaction of aqueous silica and dolomite (R2) forming isolated fo-skarns or after diopside + dolomite (R3) bordering the diopside skarns. The formation of metasomatic reaction veins during fluid infiltration is a well-established concept (e.g., Bucher-Nurminen, 1981; Bégué et al., 2019). In addition, the metastable formation of forsterite directly from dolomite and silica was previously reported by Müller et al. (2004) and Ferry et al. (2011).

$$2Dol + SiO_{2(aq)} = 2\,Cal + Fo + 2CO_2 \quad (R2)$$

$$3Dol + Di = 4Cal + 2Fo + 2\,CO_2 \quad (R3)$$

The outer phlogopite zone that borders fo-skarns comprises recrystallized dolomite and phlogopite with interstitial calcite (Fig. 10d). The transition from the forsterite zone to the phlogopite zone can be explained by the propagating reaction front lowering silica activity that leads to the partial dissolution and reprecipitation of the dolomite + calcite. The remaining amount of Si and other elements dissolved in the fluid (e.g., K, Fe, F) were incorporated in the phlogopite crystallizing along grain boundaries of the carbonates.

There is textural evidence documenting the sequential development of diopside, followed by forsterite + calcite and dolomite + phlogopite + calcite. In the zoned skarns, the formation of forsterite was a consequence of changes in either fluid composition or fluid flux. The skarn formation itself is inherently linked to physicochemical conditions and the amount and composition of the infiltrating fluid and thus, the spatial and field observations can be used to decipher the infiltration history recorded in the transition from diopside skarns to forsterite skarns. However, at least two main alternative interpretations can be used to explain the observed sequence.

The observed sequence could be explained by changes of the effective fluid flux (Fig. 15; Scenario 1), i.e., the amount of fluid flux over time during the infiltration event governing the effective water-to-rock ratio (W/R). While the effect of scale- and path-dependent W/R ratios have been successfully used to explain spatial variations in the amount of oxygen isotope shifts observed in hydrothermal systems (Bowman et al., 1987), a similar concept could be envisaged for temporal changes within a propagating reaction front. Here, a very limited amount of fluid resulting in a high molar fraction of CO_2 in the fluid ($X(CO_2)$) leads to formation of diopside by the breakdown of dolomite and aqueous silica (Fig. 13a; arrow 1). The system is initially internally buffered at high $X(CO_2)$ values (>0.8) requiring high Si-activities between 0.9 and 1 to form diopside (Fig. 13a; arrow 1). At these conditions, slightly lower $X(CO_2)$ values would result in the formation of prograde tremolite (Fig. 13a), which is not observed in the skarns. Subsequently, forsterite crystallization could be facilitated by continued fluid infiltration or subsequent pulses increasing the effective fluid flux, lowering the $X(CO_2)$ and shifting the system into an externally buffered regime at low $X(CO_2)$ conditions (Fig. 13a; arrow 2). The formation of forsterite from diopside and dolomite can occur at approximately the same temperature (~600°C), but at lower $X(CO2) < 0.06$ and $a(SiO2) < 0.15$ (Fig. 13a; arrow 2). Such a 'dry' heating stage with subsequent infiltration causing a shift in mineral reactions has previously been reported in contact aureoles involving impure dolomites (Müller et al., 2004).

In a second scenario (Fig. 15; Scenario 2), the observed sequence of diopside – forsterite – dolomite could be explained by constant fluid flux at low $X(CO_2)$ conditions and variable $aSiO_2$ (Fig. 15; S2). In this context, diopside would be formed first at low $X(CO_2)$ ($0.06 < XCO_2 < 0.17$) and low silica activity ($0.15 < aSiO_2 < 0.35$; Fig. 13a; arrow 3). The subsequent formation of forsterite can be explained by limited Si-mobility along the propagating reaction front (Fig. 13a – arrow 2; Fig. 13b – arrow 4) as suggested by Bégué et al. (2020). We note that it is also possible that this reaction could result from cooling (e.g., Fig. 13b – arrow 5; Fig. 13c – arrow 6). However, it is unlikely that a significant temperature drop would occur within a few centimetres during the formation of the zoned di-fo-skarns. On the other hand, the Si-concentration of the igneous fluid is indeed likely to be limited depending on its solubility and composition of the igneous rock it has equilibrated with before infiltration into the country rocks. We note that the dolomitic marbles contain minor silicate phases. Their conversion to skarn would require either substantial SiO_2 concentrations (very large volume reduction of the dolomite accompanying skarn formation) or large time-integrated fluid fluxes (TIFF – see Baumgartner & Rumble, 1988) if SiO_2 is introduced by an infiltrating igneous fluid.

In concluding this section, we note that the succession of zoned skarn formation starting with diopside followed by forsterite + calcite can be explained in two ways regarding the effective fluid flux but both result in variations in $aSiO_2$ and XCO_2 conditions. Additionally, we highlight that the observed heterogeneity of the "isolated" diopside or forsterite only versus "zoned" diopside-forsterite-skarns can also be explained by the process of variable fluid flux and composition. While additional geochemical data such as isotope signatures, mass balance constraints, estimates of time integrated fluid fluxes are needed to quantitatively answer some of the open questions regarding the infiltration history, such an analysis would be beyond the scope of this conceptual paper and will thus be addressed in follow-up contributions.

7.2.2. Hydrothermal veins and breccias and skarn retrometamorphism: cooling of the granitic complex and late fluid circulation leads to serpentinization and chloritization

After the final magmatic intrusions crystallized at c. 557 Ma and temperature dropped, the host rocks, skarns and A1 and A2 apophyses started to deform in a brittle manner (Fig. 14c). Late-cooling granites and pegmatites are interpreted as the source for H_2O-rich fluids that infiltrated brittle structures and previous pathways (Fig. 6d and 14c). Hydrothermal chloritization of biotite in granodiorites of the granitic complex occurred at c. 300°C (Reis et al., 2017; Hoerlle et al., 2023). We interpret that the serpentinization of skarns (Fig. 5e) occurred at similar conditions because the calcite-chlorite-veins are bordered by antigorite and calcite in the host rock and temperature ranges for serpentinization and chloritization are similar. Silica and water-rich fluids use faults, fractures and marble-skarn interfaces as pathways leading to the serpentinization of forsterite and diopside (Fig. 5e and 14c) according to reactions 4 and 5. Fully serpentinized skarns are symmetrically bordered by massive green antigorite marbles up to a few meters (e.g., Fig. 5e).

$$3Fo + 2SiO_{2(aq)} + 4H_2O = 2Atg \text{ (R4)}$$

$$3Di + 6H^{+}_{(fluid)} = Atg + 3Ca^{+}_{(fluid)} + H_2O + 4SiO_{2(aq)} \text{ (R5)}$$

$$3Dol + 4SiO_{2(aq)} + H_2O = Atg + 3Cal + 3CO_2 \text{ (R6)}$$

In both reactions, the volume change of the solids is positive. Additionally, at 300°C the serpentinization rate is highest (Martin & Fyfe, 1970). Fracturing occurs because the higher the reaction rate, the faster the volume of affected rock increases and there is little time to accommodate the stress resulting from volume increase (Jamtveit & Hammer, 2012). Serpentinization of the skarn assemblages is more intense near faults (<100 m) which indicates high fluid flux through the brittle structures. Serpentinization resulted in positive feedback between reaction-driven cracking and fluid infiltration that replaces all the prograde silicate assemblages of the skarn (Fig. 5e). Remaining fluids infiltrate into the adjacent cracked dolomites leading to the formation of antigorite and calcite from dolomite and aqueous siliceous fluids (R6). Therefore, the second metasomatic stage corresponds to a retrogressive stage and differs from the prior stages associated with the main magmatic phase of skarn formation.

7.3. Heterogeneity and asymmetry in metasomatic rocks: evidence of localized and heterogeneous fluid flow

The skarn-forming flow paths comprise mainly contrasting lithological contacts such as apophysis-marble interfaces (Figs. 3b-d), S_2 foliation planes within the carbonates (Figs. 3b) and fold hinges (Fig. 3d). Thus, the arrays of isolated diopside and forsterite skarns as well as the zoned diopside + forsterite skarns (Fig. 14a) are interpreted to be formed due to fluid flow at preexisting weak surfaces in addition to structurally controlled areas in the marbles or contacts (Fig. 14b). The asymmetry of skarns bordering apophyses (e.g., Fig. 3c) and the lack preferred occurrence of skarns in the upper or lower borders of the apophyses indicate that the fluid flow was localized and very heterogeneous. Therefore, the fact that locations of skarn formation are very heterogeneously distributed and that the size of skarns are highly varied require an a-priori highly heterogeneous fluid flow scenario where fluid availability is limited and heterogeneous in space, volume, and composition. These observations therefore are consistent with a one fluid flux event, with general limited fluid flux which results in local variability in fluid volume and associated composition as well as fluid ingress location.

Lithological and structurally controlled fluid flow during metamorphism and deformation is a well-acknowledged phenomenon (e.g., Skelton et al., 1995; Pitcairn et al., 2010). A similar forsterite-calcite assemblage formed parallel to carbonate foliation has been previously reported as the result of fluid flow and metasomatism along foliation-parallel deformation enhanced permeability by Holness (1997). Formation of pinch-and-swell structures, boudinage and folding enhanced the porosity at these interfaces and created positive feedback of deformation and fluid influx during the S_2 forming event. Brittle failure as a necessary part of both boudinage and pinch-and-swell structures was demonstrated by Gardner et al. (2015). The occurrence of diopside and forsterite skarns in sigmoidal extension veins (Fig. 2g) and along the fold hinge zones (Figs. 3a and d) suggests a S_2 synkinematic origin. Additionally, microstructures show that the forsterite and phlogopite zones are oriented parallel to the diopside skarn pinch-and-swell boundaries (Fig. 10a). Yet, recrystallization of dolomite “adjusting” its orientation parallel to the fluid pathways in the phlogopite zone suggests that the recrystallization was fluid-mediated as reported similarly by Holness (1997). We note that due to strength contrast between pyroxene and olivine diopside can behave as brittle and forsterite as ductile during the same deformation event. Coarse-grained forsterite and calcite are found in strain shadows (Fig. 10a and b) suggesting that they likely formed synchronous to the deformation event that resulted in boudinage and pinch-and-swell structures. Field observations and microstructures also suggest that as the diopside skarn bands broke brittle and that fluid infiltration led to forsterite and calcite crystallization within the fractured diopside grains (Figs. 4b-c and 10a). Hence the relative timing with earlier diopside followed by forsterite + calcite yet formed during a single event (Fig. 14b).

In the second metasomatic stage (hydrothermal veins and breccias), subvertical faults and fractures cross-cutting previous structures created new pathways for fluid flow (Fig. 14c). Fault zones are structures for fluid flow and act as localized conduits (e.g., Dipple & Ferry, 1992; Caine et al., 1996). The calcite-chlorite-sulphide veins and breccias in the granitic complex wallrocks (Figs. 5a,c and e) indicate fluid flow associated with the brittle structures (Fig. 14c). However, the serpentinization of skarn assemblages suggest that the fluids also used pre-existing pathways (Fig. 5e).

In summary, fluid flow patterns throughout the metasomatic stages foresee: (i) fluid flow along foliation planes, lithological boundaries and through axial zones in the first stage (Figs. 2d; 3a-c and 14b) and (ii) hydrofracturing and retrogression associated to fluid flow through fractures and fault zones in the second stage (Figs. 5a-c and 14c).

7.4. Using localized metasomatic reactions to decipher intrusion history: challenges and opportunities

Magmatic systems where fluid source, deformation, geometry, and timing constraints of the pluton are complex can be challenging to decipher and thus restrain the description of the sequence of events (e.g., Caçapava do Sul Granitic Complex). The different metasomatic rocks formed after the interaction of the Caçapava do Sul Granitic Complex and the marbles of the Passo Feio Metamorphic Complex helped to reveal different stages of the history of the granitic complex. Contrasting emplacement models were proposed, including a diapir-like (Nardi & Bitencourt, 1989), a sheet-like intrusion (Fragoso-César, 1991), a lens-shaped syntectonic batholith (Fernandes et al., 1992) and an intrusion along a fault-bend-fold of a right lateral strike-slip shear zone (Costa et al., 1995). However, the study of the metasomatic rocks formed at different stages supported by field relationships, petrography and geochronological data suggests that the granitic complex was likely assembled by several pulses during a c. 21 My time interval, at least. Additionally, skarns formed during different deformational regimes suggest that the first intrusions (A1) were formed under an extensional regime before c. 578 Ma followed by folding and affected by the heat and fluids of subsequent felsic magmatism from 578 Ma until c. 557 Ma, marking the reduction of tectonic activity and the end of magmatism (Fig. 14b-c). Our findings agree with the proposals that large igneous bodies can be formed by the protracted or incremental supply of magma build up over millions of years (e.g., Petford et al., 2000; Coleman et al., 2004; He et al., 2018; Tichomirowa et al., 2019).

Field and petrographical recognition of incrementally assembled plutons is difficult because conditions can prevail near the original magmatic temperatures for a long time, potentially obscuring pristine contacts between individual increments (Bartley et al., 2008). In this contribution, we have shown that studying the metasomatic reactions can be useful to unveil different stages of the intrusion history of a complex magmatic body. This is particularly elucidative when carbonate rocks are present near the intrusion resulting in the formation of skarns. These rocks form distinct microstructures and mineral assemblages that can be related to the different stages of a pluton crystallization (Meinert et al., 2005). However, this is challenging because working with multistage fluid-rock interaction requires dealing with complicated overlapping of processes that can partially or totally erase previous features.

In addition to the field relations and microstructures, dating minerals formed or reset during metamorphism and fluid infiltration (e.g., apatite and titanite) is a valuable tool in deciphering the timing constraints of fluid circulation during magmatic emplacement, even if they generally record the latest magmatic or fluid infiltration event in those rocks. Yet, precise dating of all metasomatic stages is impracticable, especially in magnesian skarn systems where the lack of datable phases is common. In calcic skarn systems, however, the direct dating of a metasomatic phase is achievable mainly when grossular-andradite garnet is present (e.g., Deng et al., 2017; Gevedon et al., 2018). Identifying precise intervals and duration of metasomatic processes in magnesian skarn systems remains challenging whereas integrated studies of magmatic zircon of the causative intrusion and metasomatic phases in metamorphic rocks provide a timespan for the pluton assembly. Finally, studying the metasomatic reactions commonly observed in the host rocks and apophyses of a magmatic complex provides useful insights on deformation and timing of pluton assembly and associated fluid activity.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Description:

Table S1. Results of LA-ICP-MS zircon U–Pb analysis for A1 mafic apophysis (DB-G1Z sample)

Table S2. Results of LA-ICP-MS zircon U–Pb analysis for A2 felsic apophysis (DB-G2Z sample)

Table S3. Results of LA-ICP-MS titanite U–Pb analysis for A1 mafic apophysis (AT-Z-01 sample)

Table S4. Results of LA-ICP-MS apatite U–Pb analysis for A1 mafic apophysis (AT-Z-02 sample)

Table S5. Results of LA-ICP-MS apatite U–Pb analysis for A1 mafic apophysis (AT-Z-03 sample)

Figure S6: Additional calculated Schreinemarkers diagrams showing the effects of variations of T, P and $aSiO_2$ on relevant diopside and forsterite forming reactions and stability fields

FIGURE CAPTIONS

Fig. 1: Location of the CSGC and PFMC in the Sul-riograndense shield, southern Brazil. (a) Tectonic domains of the Sul-riograndense Shield (TT: Tijucas Terrane; SGT: São Gabriel Terrane; PB: Pelotas Batholith; CB: Camaquã Basin; TQ: Taquarembó Terrane). (b and c) Geological map and cross-section of the PFMC and CSGC area showing main structural data and sampling locations.

Fig. 2: General field relations and structures of the dolomitic marbles of the PFMC and igneous apophyses of the CSGC. (a) General view of the marble quarry in the AT area showing folded marble (white dashed lines) forming major recumbent folds and concordant to subconcordant intrusions of A1 felsic and mafic apophyses; truck (approximate height 5 m) for scale. (b) Folded parallel intrusions of A1 apophyses with sub-horizontal N-S axis in the DB area; person (1.8 m) for scale. (c) Outcrop photo (top) and detailed sketch (bottom) of folded A1 mafic apophyses parallel to the subhorizontal N-S trending axial plane in the CL area. (d) Outcrop photo (top) and detailed sketch (bottom) of the A1 mafic and felsic apophyses parallel to the marble foliation and synkinematic di-fo-skarn formation at the termination of the mafic apophysis in the CL area; notepad (25 cm) for scale. (e) tight recumbent isoclinal fold in the dolomitic marble and intrusion of A1 mafic and felsic apophyses parallel to the axial plane in the AT area; (f) intercalation of high-strain "mylonites" and low-strain layers highlighting the S_1 foliation in the marbles; coin (diameter 3 cm) for scale. (g) tension gashes filled with di-fo-skarns in a brittle-ductile shear zone parallel to the axial planes (S_2) of marble folding in the CL area; compass for scale.

Fig. 3: Outcrop scale relations of A1 and A2 apophyses and associated skarns. (a) Outcrop photo (left) and detailed sketch (right) of diopside skarns in pinch-and-swell structures bordered by forsterite skarns formed perpendicular to irregular terminations of A2 felsic apophyses in the DB area. Location of the representative microstructures of the

zoned skarns in Fig. 10a marked by red rectangle. (b) Outcrop photo (left) and detailed sketch (right) of forsterite skarns formed in lithological contacts and foliation-parallel fractures within the marbles from fluids released from the pegmatitic portion of a A2 felsic apophysis. Yellow arrows indicate fluid pathways and possible flow direction. Stars in the left side image indicate the location of geochronological samples. Hammer (~40 cm) for scale. (c) Asymmetric skarn formation bordering mafic apophysis in the AT area. White lines indicate apophysis-skarn boundaries; red lines indicate the boundary between diopside and forsterite skarns. Apophysis thickness of approximately 20 cm. (d) Folded mafic apophysis and associated zoned skarn formation at CL area; hammer (~35 cm) for scale.

Fig. 4: Field aspects of skarns. (a) Lenticular di- and fo skarns parallel to S_1 foliation of the marbles; diopside pinch-and-swell in high strain area; Brown colors indicate “crushed” unconsolidated fine-grained carbonates; hammer (40 cm) for scale. (b) Zoned asymmetric di-fo-skarns with broken diopside boudin/pinch-and-swell structure bordered by forsterite and phlogopite zones; blue pen lid (4 cm) for scale. (c) Outcrop photograph (left) in DB area and detailed sketch (right) showing contrasting shapes and grain sizes in zoned skarns caused by strain contrast; broken diopside in pinch-and-swell structure bordered by coarser forsterite (lower strain areas) versus thin elongate diopside band bordered by fine grained forsterites in DB area. Note fo-cal within diopside fragments and dashed lines indicating local fractures in the pinch-and-swell structure.

Fig. 5: Macroscopic features of calcite-chlorite-sulphide veins and fully serpentinized skarns. (a) Outcrop photograph (left) and detailed sketch (right) showing calcite-chlorite-sulphide veins bordered by antigorite and calcite perpendicular to marble S_1 foliation; veins hosted within green antigorite-marbles with primary antigorite in a calcite-dolomite matrix located near NW-SE subvertical fault zone in the CL area. (b-c) Calcite-chlorite stockworks bordered by antigorite + calcite reaction fronts; 6 cm pen lid for

scale. (d) Cal-chl-sulphide breccia with marble and coarse calcite fragments cemented by chlorite and sulphides; CL area; coin for scale. (e) fully serpentinized di-fo-skarns and antigorite-marbles.

Fig. 6: Macroscopic features of A1 and A2 apophyses. (a) Composite A1 mafic-felsic apophysis with pinch-and-swell felsic enclaves in A1 mafic apophysis (AT area); hammer (~45 cm) for scale; (b) A2 felsic apophyses with mafic enclave and synmagmatic folding; (c) Detail of the A2 felsic rock with elongate K-feldspar grains and thin biotite layers defining the foliation indicated by white dashed lines; (d) Thick and late felsic intrusion (late A2) crosscutting A1 and A2 tabular apophyses.

Fig. 7: Microstructures of A1 mafic apophyses: (a) Photomicrograph of a bt-pl-hbl schist showing spaced foliation with intercalation of plagioclase and hornblende aggregates separated by discontinuous lenticular aggregates of biotite; chloritized biotite in a micro shear zone in the right side of the image; scale bar: 5 mm; PPL. AT area (b) Wide photomicrograph of pl-act-bt schist showing sigmoidal biotite intercalated with aggregates of plagioclase and actinolite marking S_2 foliation of the mafic apophysis, subtle crenulation (black dashed lines); scale bar: 5 mm; PPL; CL area. (c) Photomicrograph of a pl-bt-kfs-amp schist showing preferred orientation of biotite and elongated actinolite marking the S_2 foliation; short prisms of hornblende; subhedral titanites in the grain boundaries of biotite with K-feldspar or amphiboles; AT area; scale bar: 0.5 mm; XPL. (d) Photomicrograph of a pl-bt-act schist showing spaced foliation marked by intercalation of anastomosing biotite and elongate actinolite aggregates with small (<0.2 mm) grains of plagioclase in between the amphiboles. AT area; scale bar: 0.5 mm; XPL.

Fig. 8: Backscattered electron (BSE) images of representative microstructures and highlighted accessory phases of A1 mafic apophyses; in yellow: titanite; in red: apatite. (a) Microstructures of pl-bt-kfs-hbl-act showing subhedral titanite included in biotite aggregates, small rounded grains of titanite included in hornblende and rounded and

anhedral titanite in the grain boundaries of biotite with K-feldspar, plagioclase or amphibole; sample AT-Z-01; AT area; scale bar: 0.25 mm. (b-c) Microstructures of pl-bt-act schists showing apatite included in actinolite, next to plagioclases and included in plagioclase; samples AT-Z-02 and AT-Z-03, respectively; AT area; scale bar: 0.25 mm. (d) Internal structures and inclusions of titanite grains; sample AT-Z-01; AT area; scale bar: 100 μm.

Fig. 9: Microstructures of A1 and A2 felsic apophyses. (a) Photomicrograph of a A1 felsic apophysis showing a fine-grained quartzo-felspathic matrix and abundant biotite. Scale bar: 0.5 mm. XPL. (b) BSE image of A1 felsic apophysis showing preferential orientation of biotite in a Kfs-qz-pl matrix. Scale bar: 0.2 mm. (c) Photomicrograph of a hbl-bt-granodiorite (A2) showing mirmekites (green arrow); quartz with sutured grain boundaries (red arrows) and undulose extinction (blue arrows); cross-polarized light (XPL); scale bar: 0.5 mm; sample DB-G2Z from DB area shown in Fig. 3b. (d) Photomicrograph of a bt-monzogranite (A2) showing K-feldspar porphyrocrysts with lobate boundaries, quartz with undulose extinction (blue arrows) and sutured boundaries (red arrows) from AT area. Scale bar: 0.5 mm. XPL.

Fig. 10: Microstructures of a zoned di-fo-skarn, similar to the microstructures illustrated in Fig. 3a at a smaller scale. (a) general view of the skarn zones in a thin section scale, dashed white lines indicate location of Figs. 10b-d; scale bar: 5 mm, XPL; (b) di and coarse euhedral fo (~4 mm) in equilibrium with a cal matrix in a strain shadow zone; rounded tr inclusions in di; subhedral py in the cal matrix; scale bar: 0.5 mm. (c) fo- zone with fine-grained rounded fo arrays (<0.2 mm) in cal matrix and coarser fo (~0.5 mm) partially replacing the di; scale bar: 0.5 mm, XPL; (d) phl- zone with oriented phl aggregates, recrystallized dol and anhedral interstitial cal. XPL.

Fig. 11: Concordia diagrams showing U-Pb geochronology results for zircons from felsic and mafic apophyses and respective CL images of representative zircon grains of

each sample (a) A2 felsic apophysis magmatic age, hbl-bt granodiorite sample DB-G2Z, location in outcrop shown in Fig. 3b. (b) A1 mafic apophysis inherited zircon ages, sample DB-G1Z, location in outcrop shown in Fig. 3b; and (c) Magmatic and inherited zircon grains from A2 felsic apophysis, sample DB-G2Z. (d) Inherited zircon populations from A1 mafic apophysis, sample DB-G1Z. Laser ablation spot analyses are identified by number (refer to tables S1-S2 for results) on the zircon CL images in (c)-(d).

Fig. 12: Tera-Wasserburg diagrams showing U-Pb isotope analysis of (a) titanite and (b-c) apatite from A1 mafic apophyses.

Fig. 13: Calculated Schreinemarkers diagrams showing the effect of temperature, XCO_2 and SiO_2 activity on relevant diopside and forsterite forming reactions and stability fields and possible paths for the different interpretations described in the text. Arrows 1 to 4 represent the changes in effective fluid flux interpretation where 1 and 2 refer to variable XCO_2 at relatively high $aSiO_2$, arrows 3 and 4 refer to the changes in $aSiO_2$ and gray arrows 5 and 6 indicate a unlikely but possible cooling path at constant flux at low XCO_2 and $aSiO_2$. S1 = scenario 1; S2 = scenario 2.

Fig. 14: Schematic evolution model for metasomatic stages associated to the intrusion of the syntectonic CSGC. (a) A1 mafic and felsic apophyses intrusion into parallel to marble foliation S_1; estimate age between 600 and 580 Ma, related to extensional regime (b) Metasomatic stage 1: shift to a transpressional regime resulting in folding of the marbles and A1 apophyses; intrusion of A2 felsic apophyses; metamorphism of A1 mafic apophyses; formation of structurally-controlled diopside and forsterite skarns within dolomitic marbles by infiltration of SiO_2-bearing aqueous fluids released from cooling felsic apophyses at c. 578 Ma. (c) Metasomatic stage 2: final assembly of the magmatic complex after decrease in magmatic activity; cooling and brittle fracturing of the complex and associated wallrocks; infiltration of aqueous fluids released from final granitic bodies and pegmatites causing serpentinization of skarn assemblages, chloritization of biotite in felsic

and mafic apophyses and formation of calcite-chlorite-sulphide hydrothermal veins and breccias near subvertical faults at c. 557 Ma.

Fig. 15: Schematic sketch showing the evolution of the decisive parameters temperature, $X(CO_2)$ and SiO_2 activity for the different interpretations of the skarn sequence. The right-side diagram illustrates the development of the fluid flux over time. S1 = Scenario 1; S2 = Scenario 2.