

Mineral assemblages and temperature associated with Cu enrichment in the Seival area (Neoproterozoic Camaquã Basin of Southern Brazil)

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- 1 Mineral assemblages and temperature associated with Cu enrichment in the Seival
- 2 area (Neoproterozoic Camaquã Basin of Southern Brazil)
- 3
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- 19

20 Abstract

- 21 The Neoproterozoic sequence of volcanic rocks in the Camaquã Basin included in the
- 22 Lavras do Sul Shoshonitic Association hosts disseminated Cu deposits. The volcanic
- 23 sequence in the Seival Mine area includes andesitic lava flows, lapilli tuff, volcanic
- 24 agglomerate and andesitic dikes with pervasive alteration. The hydrothermal alteration is
- 25 interpreted to be a product of late-magmatic fluids or the mixing of magmatic with
- 26 meteoric fluids or basinal brines. The late–magmatic hydrothermal system started after
- volatile oversaturation and degassing in a magmatic system, which was partially segregated
- 28 into vesicles. The similar REE contents in the andesine–labradorite and albite indicate that
- 29 the fluid temperatures ranged from 600 to 250 °C. The crystallization of titanite and Fe-
- 30 clinochlore to Mg–chamosite followed the albitization process. The temperature range
- 31 associated with the chloritization process was estimated using a chlorite geothermometer

and varied from 251 ± 56 to 183 ± 39 °C. The precipitation of Mg-saponite and smectite-32 33 rich chlorite/smectite mixed-layers in some andesitic lava flows and the precipitation of 34 quartz, calcite, barite and hematite in fractures suggest fluid circulation with temperatures 35 lower than the chloritization process. The alteration minerals are represented by chlorite 36 and albite associated with pyrite-chalcopyrite, while chlorite/smectite mixed-layers and 37 barite or hematite are associated with bornite-chalcocite-covellite. Thermodynamic 38 calculations confirm the potential coprecipitation of pyrite-chalcopyrite with chlorite and 39 albite. The occurrence of bornite-chalcocite-covellite and barite seems to be favored by 40 low-temperature chlorite/smectite with neutral to mildly acidic water influx. Consequently, 41 albitization and the process of chloritization at high temperatures (> ca. 251 ± 56 °C) can be 42 used as an exploration guide for primary pyrite-chalcopyrite enrichment, and 43 chlorite/smectite at low temperatures (ca. 250 to 50 °C) can be related to bornite-

44 chalcocite–covellite or the process of Cu enrichment.

45 Keywords: Late–magmatic and hydrothermal alteration; Albitization; Chlorites.

46

47 **1. Introduction**

48 The Neoproterozoic Camaquã Basin and its associated igneous rocks contain significant 49 Au, Cu and Ag ore deposits, such as the Uruguay–São Luiz mines and the Lavras do Sul 50 Mining District (Remus et al., 2000; Bongiolo et al., 2011; Renac et al., 2014). In the 51 central-western section of this basin, volcanogenic (Lopes et al., 2014; Fontana et al., 52 2017) and plutonic rocks (Mexias et al., 2005) show pervasive alteration described as late-53 magmatic albitization and hydrothermal alteration with the influx of meteoric fluids 54 (Mexias et al., 1990a, 2005; Bongiolo et al., 2011; Fontana et al., 2017). The largest Cu 55 deposit in this basin is the Camaquã Mine, which is hosted in a Neoproterozoic sedimentary sequence and was exploited from the 18th century until 1996 (Remus et al., 2000; Laux et 56 57 al., 2005; Renac et al., 2014). This exploited deposit has an ore reserve of ~30.8 Mt with an 58 average Cu grade of ~1.06%, which is manifested as massive veins, stockworks and 59 disseminated chalcopyrite, pyrite, bornite, chalcocite, gold, silver and hematite. The 60 extrusive and intrusive rocks from the Lavras do Sul Mining District (Mexias et al., 2007), 61 which are located on the central-western rim of the Camaquã Basin, host nineteen Au and 62 Au–Cu deposits that were exploited during the same time frame (Bongiolo et al., 2011).

63 The ore zones consist of quartz and sulfide-rich quartz veins (Mexias et al., 2005) 64 associated with wall-rock alteration characterized by 'sericite', chlorite, pyrite and 65 chalcopyrite (Bongiolo et al., 2011). In the vicinity of the Lavras do Sul area, the 66 volcanogenic sequence in the Seival area hosts Cu-Ag deposits (Reischl, 1978; Lopes et 67 al., 2014). The different mines yielded ca. 0.20 Mt of Cu-ore with an average grade of 68 ~1.40%. The chalcopyrite, pyrite, chalcocite, bornite and covellite sulfides occurred in 69 association with chlorite, hematite, calcite, barite and quartz disseminated in andesitic 70 lapilli tuff and volcanic agglomerates or along fault planes cutting the volcanic sequence. A 71 recent study on the Seival Mine (Fontana et al., 2017) improved current knowledge about 72 the clay minerals in these ore deposits. Fontana et al. (2017) described the zoning and 73 lithotypes with the predominant occurrence of smectite, chlorite/smectite mixed-layers, 74 chlorite and corrensite, and suggested that the base-metal deposition was related to the 75 late-magmatic process of albitization and high-temperature hydrothermal alteration. Later 76 low-temperature hydrothermal alteration represented the mixing of magmatic and meteoric 77 fluids. Both albitization and chloritization processes were observed in the granite-related 78 epithermal systems of the Lavras do Sul area (Mexias et al., 2007; Bongiolo et al., 2011) 79 and the Camaquã Mine (Laux et al., 2005; Renac et al., 2014). A similar alteration 80 mineralogy in the vicinity of the Lavras do Sul Intrusive Complex, located 10 km west of 81 the Seival area, suggests that the Lavras do Sul porphyry–epithermal system contributes to 82 the alteration of the andesitic rocks and ore deposition in the Seival area, as also occurs in 83 the Potrerill Cu-Mo porphyry deposits and El Hueso Au epithermal deposits (Sillitoe, 84 1991; Marsh et al., 1997).

Consequently, this study focused on the chemical signatures of albite and chlorite to smectite in the hydrothermal alteration products. The petrographic and chemical analyses of the minerals were used to estimate the temperatures and bracket temperatures of late– magmatic to hydrothermal alteration. Petrographic observations and temperatures estimated by chlorite geothermometers were introduced into a thermodynamic model. This model was used to reconstruct the chemical conditions favorable to ore deposition in the process of base–metal migration in the Seival area.

92

93 2. Geological Setting

94 **2.1 Regional geology**

95 The Mantiqueira Province extends from the southeast of Brazil to Uruguay (Almeida 96 and Hasui, 1984; Silva et al., 2005). In the Gondwana supercontinent, the southern portion 97 of collision between the Rio de La Plata (Brazil) and the Kalahari (Africa) cratons is 98 characterized by the Sul-rio-grandense Shield (Fig. 1A) with Neoproterozoic ages. This 99 collision is represented by the Braziliano Orogeny and the opening of the Camaquã Basin 100 related to the post-collisional stage (Lima and Nardi, 1998; Gastal et al., 2005a, b). The 101 Sul-rio-grandense Shield comprises four geotectonic units: the Taquarembó Terrane, São 102 Gabriel Terrene, Tijucas Terrene, and Pelotas Batholith. Recovering these units, the 103 Camaquã Basin was considered as a succession of sub-basins (Paim et al., 2000) that 104 contains volcano-sedimentary sequences. The Maricá Group, which is represented by the 105 volcano-sedimentary rocks of the Maricá Formation, is related to a foreland retro arc-basin 106 setting (630-601 Ma; Paim et al., 2000; Borba et al., 2008). The Bom Jardim Group, in 107 which shoshonitic volcanism was emplaced during the strike-slip movement of the basin 108 (600–590 Ma; Janikian et al., 2008), is represented by the Hilário Formation. The late Santa 109 Bárbara Group (574–544 Ma; Sommer et al., 2006; Bicca et al., 2013; Almeida et al., 2012; Janikian et al., 2012; Matté et al., 2016) is mainly represented by the acidic 110 111 effusive/explosive episodes and minor basic magmatism of the Acampamento Velho 112 Formation and by the sedimentary sequences of the Santa Fé and Santa Bárbara formations (Fig. 1B). The Guaritas Group (547–535 Ma; Almeida et al., 2012; Oliveira et al., 2014) is 113 114 represented by volcanic rocks of the Rodeio Velho Formation associated with a sedimentary 115 sequence represented by the Pedra Pintada and Guaritas formations related to transtensional 116 tectonic stages (Paim et al., 2000; Almeida et al., 2012). These effusive rocks have basic to 117 intermediate sodic compositions with mildly alkaline to high-K tholeiitic affinities 118 (Almeida et al., 2012). 119 120 **INSERT Figure 1**

121

122 The volcano-sedimentary units that occur in the Seival area (Fig. 2) have dominant 123 intermediate compositions with basic and acidic end-members. The Bom Jardim Group, as 124 previously described, consists of the effusive units of the Hilário Formation in the study 126 Lavras do Sul contact suggests that the Hilário Formation is older than the Lavras do Sul 127 Intrusive Complex (Gastal et al., 2015). The Hilário Formation consists of dominantly 128 andesitic rocks represented by andesitic lava flows, lapilli tuff, volcanic agglomerates, and dikes with a shoshonitic geochemical affinity (Lopes et al., 2014; Fontana et al., 2017). The 129 130 Ar-Ar radiogenic dating of plagioclase suggests an age of 600 to 590 Ma (Janikian et al., 131 2008) that might be thermally influenced by intrusive magmas such as dikes or the Lavras 132 do Sul granitoids. The other vesicular lava flows and volcanic clastic materials are represented by the polymictic conglomerates of the Santa Fé Formation. The Acampamento 133 134 Velho Formation occurs as rhyolite dikes that cross-cut the Hilário Formation. 135 136 **INSERT Figure 2** 137 138 The granitoids of the Lavras do Sul Intrusive Complex with U-Pb ages varying from 601 to 587 Ma (SHRIMP in zircon, Remus et al., 1999, 2000; Gastal et al., 2006; Liz et al., 139 140 2009), comprise a ring structure composed of porphyritic quartz-monzonite granodiorite 141 and syenogranite to monzogranite with monzonitic intrusions in its northeastern margin 142 (Gastal et al., 2006; Liz et al., 2009). In the contact zone between the Lavras do Sul 143 granitoids and the Hilário Formation is a hectometer-thick metamorphic halo (Mexias et al.,

area (Ribeiro and Fantinel, 1978). The deformation of the Hilário Formation along the

144 1990a, b; Bongiolo et al., 2011) attesting to the thermal influence of granitoids on the145 volcano-sedimentary pile.

146

125

147 **2.2 Ore geology**

148 The Seival hosts six inactive Cu-bearing deposits and several prospects. This reserve 149 was estimated at ~0.20 Mt of ore with an average grade of ~1.40% of Cu and 10-70 ppm of 150 Ag (Fig. 3A; Reischl, 1978; Lopes et al., 2014). The ore deposits in the Seival area were 151 associated with the development of NE-SW-oriented shear zones that cross-cut the 152 Camaquã Basin (Fernandes et al., 1992; Philipp et al., 2016). The emplacement of metallic 153 mineralizations are bracketed between 600 and 580 Ma ago based on the ages of lava flows 154 (Janikian et al., 2008), tectonic activity (Gastal et al., 2015) and the Lavras do Sul 155 magmatism (Gastal et al., 2006; Almeida et al., 2012).

156 The sulfides are represented by chalcopyrite, bornite, chalcocite and covellite (Fontana 157 et al., 2017) and are part of the main Cu-bearing veins that fill fractures and faults. The 158 alteration halos are related to the distances of mineralized structures (Lopes et al., 2014; 159 Fontana et al., 2017). The mineral association of chlorite, epidote and calcite formed at 160 temperature of ~300 °C (Mexias et al., 1990b; Mexias et al., 2007; Bongiolo et al., 2011) in 161 the volcanogenic rocks of the Hilário Formation close to the Lavras do Sul granitoids. 162 The mineral assemblages allow for the characterization of hydrothermal zones 163 (Seedorff et al., 2005; Sillitoe, 2010). Propylitic alteration was related to chlorite, C/S 164 mixed-layer, hematite, titanite, calcite, barite and quartz associated with pyrite-165 chalcopyrite and chalcocite-bornite, while argillic alteration was related to smectite and 166 quartz (Fig. 3B; Lopes et al., 2014; Fontana et al., 2017). Cu enrichment was associated 167 with propylitic alteration and the formation of albite (600 to 250 °C; Fontana et al., 2019) and Mg-chamosite to Fe-clinochlore (251 to 180 °C). The late-hydrothermal veins are 168 169 composed of barite, calcite and minor proportion of veins with calcite-quartz assemblage. 170 These late precipitations represent the lowest temperatures of hydrothermal alteration (150 171 to 80 °C; Fontana et al., 2017). In the preserved parts of these inactive mines, 172 mineralization occurs as a stockwork of veins or disseminated in volcaniclastic rocks and 173 andesitic lava flows (Fontana et al., 2017). The faults, mineralized structures and dikes are 174 considered contemporaneous based on the mineralogy and alteration type. Thus, the 175 hydrothermal processes can be associated with the intrusion of NE-SW-oriented andesite 176 (Lopes et al., 2018) and local hydrothermal cells.

- 177
- 178 INSERT Figure 3
- 179

180 **3. Analytical methods**

Field work consisted of sample collection and logging of drill cores. The samples collected were representative of lapilli tuff, amygdaloidal to porphyritic andesitic lava flows and dikes. Petrographic observations of thin sections allowed the description of magmatic and hydrothermally altered crystals. The minerals, after of crushing and sieving, were separated using a magnetic separator, heavy liquids and hand–picking under a binocular microscope. Products of alteration were either collected under a binocular 187 microscope in the altered phenocrysts or identified in the clay-size fraction. These 188 petrographic observations, mineral separation and clay-size fraction were characterized by 189 scanning electron microscopy combined with energy-dispersive spectrometry (SEM-EDS, 190 Zeiss EVO LS15, 20 kV, 2.5 nA with X-Max Oxford EDS detectors, IAEA Monaco) and 191 X-ray diffraction (Siemens D5000, KaCu, 40 kV and 25 mA, Geoscience Institute-CPGq-192 UFRGS). X-ray patterns of the clay minerals were obtained in $< 0.4 \mu m$ clay-size fraction. 193 Major element composition as oxides (SiO₂, TiO₂, Al₂O₃, FeO_{total}, MnO, MgO, CaO, Na₂O, 194 F and K_2O) in minerals from thin section were quantified by electron microprobe 195 (CAMECA, SXFive model equipped with TAP, PET and LIF crystal detectors) at the 196 Geoscience Institute, Universidade Federal do Rio Grande do Sul, Brazil. The beam 197 diameter is about 10 to 4 µm with an acceleration voltage of 15 kV and 15 nA with 198 counting time per element of 10 sec and background counting times of 5 sec per element. 199 Chemical calibrations were performed on albite, jadeite, diopside, sanidine, rutile, 200 rhodonite and hematite standards mounted in epoxy resin. The mineral composition in thin 201 section were calculated of atom per formula unit (a.p.f.u.) assumed the following number of 202 oxygen atoms for ideal compositions of feldspar (32), pyroxene (12), biotite (22), titanite 203 (5), smectite (22), chlorite/smectite mixed-layer (28) and chlorite (28). Charge balance of 204 structural formula was obtained by the adjustment of Fe²⁺ and Fe³⁺ proportions, including for smectite and biotite, where only Fe²⁺ was considered. Analyzes in ten thin sections were 205 206 performed to follow changes from preserved magmatic minerals to mineral transformed or 207 precipitated by the hydrothermal alteration. Based on major element compositions, 208 chemical changes will then be related to albitization and chloritization processes. The 209 complete dataset of primary and hydrothermal minerals analyzed are available in 210 Supplementary Table A–G. 211 The major element changes observed in plagioclase were completed by rare earth 212 elements (REE; lanthanides, Y and Sc) analyzes. These REEs have been measured from 213 plagioclase separates preliminary recovered for phenocrysts and the microlithic 214 groundmass subsequently recognized with different major element compositions. These 215 REE concentrations were measured from feldspar separates preliminary acid leached with 216 ultrapure HNO₃ (1N) to dissolve traces carbonates and oxides on the surface of the grains

217 separated then clean in ultrapure pure MQ water. Later, cleaned grains were then acid

218 digested in ultrapure HNO₃ (15N) and HF (20N). Inductively-coupled plasma mass

- 219 spectrometry analyzed all digested samples diluted in 1% HNO₃ solutions (ICP–MS: Elan
- 220 DRCII, Perkin Elmer at the University of Nice Sophia-Antipolis). Quantification limits are
- 221 below 50 ng/L. Element concentration was expressed as ppm and then normalized with
- 222 respect to chondrite values (McDonough and Sun, 1995). The Eu* the values of the Eu
- anomaly were calculated using $[Eu^*] = [((Eu_N)/(Sm_N \times Gd_N)^{1/2})]$ from Worrall and Pearson 223

(2001) or $[Eu^*] = [((Eu_N)/(Sm_N^2 \times Tb_N)^{1/3})]$ from Lawrence and Kamber (2006). 224

225 The different mineralogical and chemical data of magmatic minerals were used with the 226 petrogenetic model (MELTS software modeling; Ghiorso and Sack, 1995) to reconstruct 227 magmatic conditions. The magmatic and hydrothermal minerals were combined in a 228 thermodynamic model (PHREEQC interactive; Parkhurst, 1995) to estimate the favorable 229 conditions for precipitation of hydrothermal phases and sulfides.

230

231 4. Results

232

4.1 Textures and petrographic observations

233 The host rocks of the Cu deposits in the Seival area are predominantly and esitic lava 234 flows and lapilli tuff (Fig. 4A) to volcanic agglomerates with rounded andesitic pyroclasts. 235 Their aphyric groundmasses are dark to glassy and green with disseminated microlites of 236 plagioclase and fragments of pyroxene. Amygdaloidal and porphyritic andesitic lava flows 237 are predominant in the southern and northeastern parts of the Seival area and are in contact 238 with the Santa Fé Formation (Fig. 2). Subvolcanic rocks have andesitic (Fig. 4B) to 239 trachyandesitic compositions with feldspar phenocrysts, dominant pyroxene and scarce 240 biotite phenocrysts.

241 Most of the rocks are intensively fractured and brecciated, particularly those with 242 higher Cu sulfide contents. The andesitic pyroclasts in the lapilli tuff show vesicles or 243 amygdaloids. The amygdaloidal groundmass in the lapilli tuff consists of fragments of 244 igneous plagioclase and pyroxene. The petrographic observations of pyroxene revealed the 245 replacement by clay minerals and calcite or intergranular spaces filled by clay minerals, 246 quartz, calcite, titanite, pyrite, chalcopyrite, and minor hematite (Fig. 4C).

247 Porphyritic andesitic lava flows have phenocrysts of plagioclase and clinopyroxene 248 in a trachytic groundmass with oriented plagioclase. Andesitic dikes host subhedral grains

of feldspars further identified as plagioclase with rims of K–feldspar (Fig. 4D) and phenocrysts of pyroxene. Some trachyandesitic dikes have subhedral phenocrysts of plagioclase, pyroxene and biotite. Some plagioclase and biotite phenocrysts have inclusions of apatite, zircon (50 to 200 μ m) and titanite, while the oxidized groundmass contains hematite. The titanite grains occur as euhedral grains associated with biotite and pyroxene and as anhedral grains of smaller granular agglomerates in the altered groundmass.

As previously described (Lopes et al., 2014; Fontana et al., 2017), the Hilário volcanic sequence in the studied area is pervasively altered to clay minerals, calcite, barite and quartz. The original igneous mafic minerals and different groundmasses have a light green material recognized as chlorite/smectite mixed–layer (Fig. 4E). Albite, chlorite and sulfide occur in the more altered rocks with traces of calcite and specular hematite, and euhedral or agglomerates of titanite occur with albite and microscopic euhedral quartz (Fig. 4F).

262 Less-altered material occurs in the amygdaloidal andesitic lava flows from the south 263 and west. Nevertheless, these lava flows are partially altered to dark clay minerals (Fig. 4G) 264 between crystals or exhibit quartz, pyrite-chalcopyrite and calcite filling vesicles. 265 Petrographic observations indicate the predominance of clay minerals associated with 266 sulfides in the intergranular porosity that are further recognized as chlorite and dominant 267 pyrite-chalcopyrite, or the association of chlorite/smectite mixed-layer (Fig. 4H) with minor pyrite-chalcopyrite and dominant chalcocite-covellite or chalcocite-bornite. The 268 269 malachite and azurite observed in the different open pits are the product of the recent 270 weathering of Cu-rich sulfides.

271

272 INSERT Figure 4

273

4.2 Major element compositions of magmatic to late-magmatic minerals and REE compositions of feldspars

- 276
- 277 lava flows and andesitic dikes are augite (Wo 0.40–0.47 En 0.32–0.41 Fs 0.12–0.28; Fig. 5A;
- 278 Supplementary Table A). According to the structural formula of augite (Table 1), the atomic

Phenocrysts and microlites or crystalloclasts of pyroxene in porphyritic andesitic

279 ratios of $[Mg/(Mg+Fe_{tot})= 0.67-0.85]$ are high and those of [Na/(Ca+Na)= 0.02-0.05)] are 280 low.

Prismatic biotite phenocrysts recognized in trachyandesitic dikes are classified as Mg–biotite with the structural formula expressed in Supplementary Table B. The less pristine Mg–biotites show slightly different compositions (Table 1), with increases in Al^{VI} (Fig. 5B) and lower contents of Fe, Mg and Mn (Table 1). The euhedral to agglomerate titanite grains (Fig. 5C; Table 1 and Supplementary Table C) are associated with albite and biotite phenocrysts, and the anhedral grains in the groundmass have similar chemical compositions.

288 The chemical compositions of feldspars were analyzed in thin section. The 289 plagioclase phenocrysts have compositions of andesine-labradorite (An 0.43-0.53 Ab 0.43-0.54 290 Or 0.03-0.05) (Table 1). Moreover, some of the andesine-labradorite phenocrysts have a thin 291 rim of K-feldspar (An 0-0.01 Ab 0-0.33 Or 0.66-1; Fig. 4B and Fig. 5D; Table 1), further described as Group I. In contrast, the microlites and phenocrysts of plagioclase 292 293 (Supplementary Table D) from altered lapilli tuff, porphyritic andesitic lava flows and 294 andesitic dikes consist of dominant albite (An 0-0.06 Ab 0.89-1 Or 0-0.10; Table 1), further 295 described as Group II. The feldspar separates were characterized by X-ray diffraction and 296 observed by SEM-EDS. The separates with traces of illite or quartz were removed from 297 further REE measurements. The total REE content of andesine-labradorite (Group I) and 298 albite (Group II) have similar patterns and are slightly higher in albite. However, the 299 andesine-labradorite (Group I) and albite (Group II) have both positive have positive Eu 300 anomalies (Group I: [Eu*]= 0.90–1.22; Group II: [Eu*]= 1.04–4.60; Table 2).

- 301
- 302 INSERT Figure 5
- 303 INSERT Table 1
- 304 INSERT Table 2

305

306 **4.3 Mineralogy and major elemental compositions of clay minerals**

Petrographic observations show "green clays" replacing pyroxene, biotite or
 feldspars that fill vesicles and intergranular porosity. Similar to Fontana et al. (2017), using
 X-ray diffraction techniques on clay-size fractions allowed for the identification of

310 dominant trioctahedral smectite and smectite-rich (C/S) in less altered andesitic lava flows, 311 as well as chlorite-rich chlorite/smectite mixed-layer and chlorite in more altered andesitic 312 lava flows and lapilli tuff. The occurrence of different clay minerals for similar andesitic 313 lithotypes suggests that hydrothermal alteration is not completely related to the primary 314 magmatic mineralogy but to the influx of external fluid. The in-situ electron microprobe 315 analyses allowed for the identification of the composition of the large chlorite flakes (Fig. 316 6) in the cleavage of andesine–labradorite and albite and the replacement of augite 317 phenocrysts or micrometer vugs in the andesitic dikes with a light green color (Table 1). Based on the Fe²⁺/(Fe²⁺+Mg) ratio, these chlorites have compositions of Fe–clinochlore to 318 Mg-chamosite (Supplementary Table E). The observed $Fe^{2+}/(Fe^{2+}+Mg)$ atomic ratios 319 between 0.47 and 0.64 suggest that values < 0.5 are Fe–clinochlore and those of > 0.5 are 320 321 Mg-chamosite. These two types of chlorite were also recognized in a regional epithermal 322 system (Fig. 7; Mexias et al., 1990b; Bongiolo et al., 2011) and distal-epithermal halo from the Camaquã Mine (Fig. 7; Troian et al., 2010; Renac et al., 2014). Low Fe²⁺/(Fe²⁺+Mg) 323 proportions are structurally compensated by tetrahedral and octahedral aluminum (Al^{IV}= 324 325 1.7 to 3.4; Al^{VI}= 2.7 to 3.11). The Fe–clinochlore to Mg–chamosite in andesitic lava flows and lapilli tuff have lower Fe²⁺+Mg atomic proportions (7.5 to 8.5; atomic ratios of 326 327 $Fe^{3+/}Fe_{tot} = 0.01$ to 0.06) than in andesitic dikes ($Fe^{2+}+Mg = 9$ to 10.1; atomic ratio of Fe³⁺/Fe_{tot}= 0.05). However, the chloritization of augite and filling of vugs reflect increasing 328 contents of Fe+Al and Fe+Mg total contents in lapilli tuff and andesitic dikes, respectively. 329 330 In addition, the Fe-clinochlore to Mg-chamosite compositions are very similar (Fig. 8A; 331 Table 1) and were described using the same structural formula.

- 332
- 333 INSERT Figure 6
- 334 INSERT Figure 7

335 INSERT Figure 8

336

The occurrence of dominant chlorite/smectite, trioctahedral smectite and corrensite
recognized by their dark green color and identified using X-ray diffraction (Fig. 8) was
confirmed by electron microprobe measurements. The smectite-rich chlorite/smectite,

340 smectite (Supplementary Table F) and corrensite (Fig. 8B and Figs. 9A–B) represent the

- 341 dominant hydrothermal phase of andesitic lava flows and andesitic dikes. The dominant
- 342 trioctahedral smectite (Fig. 8C) has a Mg–saponite composition (Table 1). The dominant
- 343 chlorite–rich chlorite–smectite (Fig., 8D; Supplementary Table G) with micrometer-scale
- 344 fan-shaped particles (Fig. 4C) occurs in altered porphyritic and amygdaloidal andesitic lava
- 345 flows. The chlorite–rich chlorite–smectite have Al^{VI} and ^{IV} contents (Al_{tot} 2.21+ 1.25 to
- 346 2.46+ 1.48 a.p.f.u.) that are higher in the porphyritic andesitic lava flows than the chlorite–
- 347 rich chlorite–smectite (Al_{tot}= 1.59+0.77 to 1.93+1.47) in the amygdaloidal andesitic lava
- 348 flows. The proportion of Fe and its valency balance are represented by changes in
- 349 tetrahedral and octahedral Al. The chlorite-rich chlorite-smectite structural formulas vary
- between porphyritic and amygdaloidal andesitic lava flows (Table 1).
- 351

352 INSERT Figure 9

353

It is possible to confirm the association of albite and chlorite minerals with Cu enrichment. The magmatic and post-magmatic stages were related to albite and chlorite crystallization, while chlorite, chlorite/smectite mixed-layer and the destabilization of sulfides were related to the precipitation of chalcocite-bornite. These mineral associations suggest a sequence of crystallization and hydrothermal alteration over time.

359

5. Discussion

361 **5.1 Chemistry of magmatic and late-magmatic minerals**

362 The volcanogenic rocks in the Seival area are interpreted as part of the Lavras do 363 Sul Shoshonitic Association (Lima and Nardi, 1998), which are related to the Lavras do Sul 364 granitoids and lamprophyres. The occurrence of lamprophyres (Lima and Nardi, 1998; 365 Almeida et al., 2012), andesitic dikes and various volcanic events in the region suggests 366 long and intense episodes of magmatism in the Seival area constrained by the dating of 367 zircon (Almeida et al., 2012; Janikian et al., 2012) between 600 ± 2 to 590 ± 6 Ma. The 368 mineralogy of andesitic rocks with andesine-labradorite, augite and Mg-biotite phenocrysts 369 and their whole-rock compositions (Lima and Nardi, 1998; Sommer et al., 2006; Lopes et 370 al., 2014) suggest a petrogenetic link with the Lavras do Sul Shoshonitic Association.

371 Petrogenetic modeling (MELTS Software: Ghiorso and Sack, 1995) used with 372 whole-rock compositions (Lopes et al., 2014) estimates a liquidus temperature of ca. 1080 373 °C. The modeling shows a sequence of crystallization initiated by calcic plagioclase 374 followed by low-Ca-pyroxene, late orthoclase and high-Ca pyroxene or biotite (ca. 800 375 °C). The stages below 800 °C include late-magmatic minerals formed by volatile-rich melt (c.f. Dixon et al., 1995). In this context, the biotites observed with the higher Al^{IV} contents 376 377 of less pristine biotite compared with the biotite phenocrysts might represent two stages of 378 biotite crystallization or slightly altered crystals. The late-magmatic stage initiated at 379 solidus temperatures (800 to 500 °C) with volatile oversaturation and the degassing of the 380 melt (c.f. Dixon et al., 1995). This interpretation is reinforced by the oxygen isotopic values of and esine-labradorite (δ^{18} O and esine-labradorite: 6.6 to 8.2 %; Fontana et al., 2019) showing 381 the magmatic signature of fluids in equilibrium with feldspars (Taylor, 1987) evolving 382 383 toward the mixing of meteoric and magmatic fluids for albite (δ^{18} O _{albite}: 14.2 to 16.2 %; Fontana et al., 2019). Consequently, presume that observed Mg-biotite formation, euhedral 384 385 F-rich titanite grains and albite are related to late-magmatic crystallization and albitization 386 processes of andesine-labradorite. According to thermodynamic modelling and the 387 literrature (c.f. Higgins and Ribb, 1976; Franz and Spear, 1985; Enami et al., 1993; Tropper 388 et al., 2002; Harlov et al., 2006; Hövelmann et al., 2010; Kaur et al., 2012) this albitization 389 process occurs at temperatures below 800 °C, presumably from ca. 600 to 250 °C. The 390 widely observed albite suggests a magmatic to high-temperature hydrothermal system 391 (epithermal-porphyry: Richards, 2003; Sillitoe, 2010 or Iron Oxide-Copper-Gold; Sillitoe, 392 2003; Williams et al., 2005; Groves et al., 2010). The alkaline and acidic fluids in these 393 systems are related to the albitization process and K-rich alteration (Perez and Boles, 2005; 394 Boulvais et al., 2007) that, to some degree, participated or started the leaching of base 395 metals from the lava (Moody et al., 1985; Perez and Boles, 2005; Hövelmann et al., 2010; 396 Kontonikas-Charos et al., 2014). Non-magmatic basinal brine has also reported in the 397 albitization process (Barton and Johnson, 1996 and 2000), such as in the Nevada porphyry, 398 IOCG deposits (Carten, 1986; Dilles and Einaudi, 1992; Dilles et al., 2000; Sillitoe, 2003; 399 Mark et al., 2006; Kendrick et al., 2007) or Chilean "Manto-type" deposits, such as 400 Michilla, with the mixing of magmatic and basinal brine (Barton, 2014). In the Seival area, 401 the change of andesine-labradorite (An 0.43-0.53 Ab 0.43-0.54 Or 0.03-0.05) to albite (An 0-0.06 Ab

402 0.89-1 Or 0-0.10) with rare K-feldspar rims on andesine-labradorite or rare illite attest to the 403 circulation of alkaline fluid. Moreover, the sizes of the quartz and calcite crystals with 404 liquid inclusions did not allow fluid inclusion microthermometry to recognize high-density 405 fluid, as in IOCG-type deposits (Reeve et al., 1990; Davidson and Large, 1998). The REE 406 patterns of albite-rich separates (Group II: $Eu^* = 1.04 - 4.60$) are similar to the whole-rock 407 (Fig. 10; Lopes et al., 2014). The more positive Eu anomaly of group II and whole-rock 408 (whole–rock: $Eu^* = 6.23$) compared to Group I (Labradorite $Eu^* = 0.90-1.20$). These 409 overall, positive Eu positive anomalies (Eu*=>1; Table 2) higher in the albite (group II; 410 Fig. 10A-B) than and esine-labradorite-rich grains (group I) seem unrealistic assuming, 411 first crystallization of Ca-feldspar then Na-rich feldspar. However, the more positive Eu 412 anomalies of whole-rock and Group II might be related to trace minerals such as apatite 413 inclusions in plagioclase, as mentioned in the petrography section and whole-rock. These 414 inclusions have not been remove totally by preliminary acid-leaching used to clean 415 feldspars of carbonates, Ca-phosphates and Fe oxides (Fontana et al., 2017). The REE 416 signature of Ca-rich feldspar would then represent a chronologically primitive signature in 417 the magmatic chamber, while, the late crystallization include dominant Na-rich feldspar 418 and phosphate traces.

419 Nevertheless, the similar
REE contents with LREE and HREE variations from 420 albites and and esine-labradorite suggest a similar source of REE (\Box REE) that was not 421 affected by fluid dilution, such as that by meteoric fluids. Therefore, the albitization process 422 in the Hilário Formation was related to the neutral to mildly acidic water circulation of Na-423 rich magmatic fluid, such as late-magmatic glass interactions with outgassing magmatic 424 fluids (CO₂ and H₂O), but these data cannot decipher between a magmatic to late-425 magmatic crystallization with the mixing of magmatic fluids and brine (e.g. IOCG: Barton 426 and Johnson, 1996 and 2000).

427

428 **INSERT Figure 10**

429

430 No mineralization model has yet been proposed for the Seival Mine. Fontana et al.
431 (2017) indicated mineralization associated with magmatic and meteoric fluids. The aligned
432 Cu–Ag ore bodies and disseminated mineralizations (see Figure 3) with similar mineral

433 assemblages (albite, chlorite, chlorite/smectite mixed-layers, chalcocite-bornite, barite, and 434 minor calcite, hematite and quartz) could be typical of epithermal deposits (Sillitoe, 2010) 435 associated with the geothermal influence of andesitic dikes or the Lavras do Sul granitoids. 436 These observations and interpretations suggest that Seival would be a superficial part of the 437 Lavras do Sul porphyry (Mexias et al., 2007; Bongiolo et al., 2011). We assumed that low-438 hematite contents in the Seival area associated with calcite in small veins and ore deposits 439 without an iron–oxide caprock are clues discarding the hypotheses of an IOCG type deposit 440 or a metallic enrichment related to weathering profile such as Gossan genetic model of ore 441 deposits.

442

443 **5.2** Clay minerals and chlorite during hydrothermal stages

444 The hydrothermal stages associated with saponite, chlorite/smectite and chlorite 445 precipitations surrounding albite suggest hydrothermal fluids of below 350 °C. Previous 446 studies (Lopes et al., 2014; Fontana et al., 2017) characterized the occurrence of Fe-Cu-447 rich sulfides associated with chlorite/smectite. The association of Cu-rich sulfides with Fe 448 -Al -Mg rich chlorite/smectite suggests that the Fe²⁺, Mg and Al contents of the clay 449 minerals are related to ore deposition (Wilkinson et al., 2015; Yoneda et al., 2016). 450 Nevertheless, the origin, chemistry and temperature of the fluids are not well characterized. 451 In the Seival area, crystallography realized by X-ray diffraction and mineral 452 chemistry obtained by electron electron microprobe analyses identified Mg-saponite 453 (smectite), chlorite/smectite mixed-layer and corrensite infilling the porosity or 454 intergranular spaces. The occurrence of dominant clay minerals with Mg-saponite, 455 chlorite/smectite and corrensite in different lithotypes was interpreted as a lithological 456 control of alteration rather than being derived from local equilibrium (Fontana et al., 2017). 457 The comparison of the major element compositions of magmatic minerals (Part 4.2), clay 458 mineral (part 4.3) and whole–rock samples (Lopes et al., 2014) provided information to 459 support this hypothesis. The predominant Fe– Mg–rich clay minerals and their 460 Fe_{tot}/Fe_{tot}+Mg atomic ratios compared to augite (0.14 to 0.27) and biotite (0.37 to 0.44) 461 indicate that Mg-saponite (0.22 to 0.27) and chlorite/smectite mixed-layers may be derived 462 from the alteration of magmatic minerals and glass. In contrast, the high Fe-clinochlore to 463 Mg-chamosite ratio (0.47 to 0.63; Supplementary Table E) suggests the addition of Fe and

464 Mg during the chloritization process. This interpretation as confirmed by mass-balance465 calculations performed by Fontana et al. (2019).

466 We estimated the temperatures of chlorites using chemical thermometers (Inoue et 467 al., 2009; Bourdelle and Cathelineau, 2015). These thermometers are the only available 468 temperature constraint considering the small sizes of the fluid inclusions (Fontana et al., 469 2017). We discarded the chemical thermometer of chlorite related to metamorphic 470 conditions and selected one determined in similar lithotypes and pressure conditions. The 471 chosen chemical thermometers use a structural formula with an uncertainty dominantly 472 controlled by the Fe valency and different octahedral layers. Assuming an error of 20% in 473 the Fe distribution, the uncertainty is approximately 50 °C in both calculations. The 474 calculated temperatures of Fe-clinochlore to Mg-chamosite (Supplementary Table E) vary 475 from 129 to 275 °C in the lapilli tuff–andesite (median= 183 ± 39 °C; n= 18) and 172 to 476 312 °C in andesitic dikes (median= 251 ± 56 °C; n= 8). Moreover, the compositional 477 changes in chlorite in the Seival area compared to those in the Lavras do Sul area (Mexias 478 et al., 1990b; Bongiolo et al., 2011) or the Camaquã Mine (Renac et al., 2014) yield 479 comparable temperatures. These different uncertainties (± 50 °C) and calculated 480 temperatures reflect chloritization below of the minimum temperature of albitization. The 481 higher temperature of chlorite associated with andesitic dikes suggests a temperature 482 related to intrusive bodies or different thermal gradients between lapilli tuff and andesitic 483 dikes.

484

485 **5.3 Hydrothermal evolution and thermodynamic modeling**

The chlorite and chlorite/smectite mixed-layers associated with sulfides are typical mineralogical assemblages of hydrothermal deposits (Barnes, 1979; Pirajno, 2009; Sillitoe, 2010). In the Seival area, different Fe–Cu –rich sulfide assemblages occur in the intergranular space or are mixed with clay minerals (Fontana et al., 2017).

Hydrothermal alteration minerals are associated with a sequence of precipitations
rather than a paragenetic assemblage, as occurs in metamorphic reactions. Therefore,
thermodynamic modeling can be erroneous when based on the assumption of an output
represented by all of the hydrothermal phases observed. Consequently, we tested the
different equilibrium conditions of the hydrothermal stage (below 350 °C) with

495 thermodynamic modeling (PHREEQC interactive; Parkhurst, 1995, rather than SUPCRIT 496 or the equivalent CHONZ Rpackage). The PHREEQC thermodynamic models primarily 497 use minerals with an initial water content and propose secondary minerals as outputs with 498 the new composition of the final fluid. In our case, reactions involved observed magmatic 499 minerals observed (feldspars: andesine-labradorite and albite and Ca-pyroxene: augite) and 500 late-magmatic minerals (biotite, titanite, Fe-titanium oxides and silica-rich glass) reacting 501 with initial fluid (low-concentration water similar to rainfall, Salve et al., 2008), and 502 carbonic fluids (CO_2 as recognized in fluid inclusions (Fontana et al., 2017). The 503 temperature domain of these calculations was bracketed by the albitization process (< 350 504 °C) and the calculations of the chlorite thermometer (120 to 320 °C). Each calculation 505 considers a molar proportion of water a hundred times higher than those of minerals and 506 fluids for varying pH values and temperatures below 350 °C. Consequently, the 507 thermodynamic changes in calculated fluids and the dissolution or precipitation of primary 508 and secondary minerals equilibrated at 350, 300, 250, 200 and 150 °C with pH and Eh were 509 adjusted for charge balance and redox conditions. These preliminary calculations indicate 510 multiple solutions with more products than were identified in the altered rocks. Therefore, 511 we forced the software to uniquely consider results with chlorite, calcite, quartz and Fe-Cu 512 rich sulfide or barite, which are here assumed to be products of hydrothermal reactions, 513 without any constraints related to their precipitation or dissolution. 514 These thermodynamic calculations were obtained for neutral (pH: 7) and acidic (pH: 515 4) initial water conditions. Regardless of the considered temperature, all final waters remained neutral for an initial fluid with a neutral pH (pH: 7 to 7.3), whereas acidic waters 516 517 changed to a neutral pH (pH 4 to 7.3). 518 The high-temperature (350 °C) calculations indicate the coprecipitation of albite 519 and titanite with the total consumption of the Ca-rich feldspars and pyroxene, but no minor 520 chlorite or smectite. The conservation of some pyroxene and andesine-labradorite observed

- 521 in the petrography and the lack of clay minerals suggests unrealistic solutions for
- 522 hydrothermal alteration forming albite with titanite and chlorite. Consequently, we forced
- 523 the precipitation of chlorites in a second data set.

- 524 For temperatures between 350 and 250 °C, the chlorite, quartz and calcite 525 associated with pyrite and chalcopyrite can be formed, whereas silica–rich glass, titanite 526 and Ti–magnetite are consumed anorthite, albite and pyroxene are partially dissolved.
- 527

528

529

– For temperatures between 250 and 150 °C, neutral or acid water dissolved magmatic minerals with predicted precipitations of chlorite, barite, calcite, quartz and hematite with bornite–chalcocite. Mg–saponite (smectite) was precipitated below 200 °C.

- Below 150 °C, the lower activities of Fe²⁺ with decreasing HS⁻/(HS⁻+SO₄) molar 530 531 ratios increased the saturation with respect to chalcocite and sulfate and Fe oxides, such as 532 barite and hematite. These calculations confirm that pyrite and chalcopyrite were probably 533 precipitated from a dominant magmatic fluid at temperatures between 350 to 250 °C. The 534 further mixing of the magmatic fluid with meteoric water or basinal brine at temperatures 535 varying from 250 to 150 °C promoted chalcocite-bornite deposition. Considering the 536 domain of barite saturation and the lack of supergene alteration or gossan profiles in this 537 region, the lower temperature of the Cu enrichment of sulfide ranged from 150 to 50 °C. 538

539 **6.** Conclusions

540 The Seival area contains hydrothermal Cu-sulfide deposits hosted in volcanic rocks 541 with a shoshonitic affinity. Interpretations based on mineralogical and chemical data 542 suggest that volatile-rich magma produced Mg-biotite, followed by late-magmatic 543 alteration with titanite and the albitization of andesine–labradorite (650 to 250 °C), as 544 suggested by the REE contents of albite. Thermodynamic modeling indicates that late 545 albitization (ca. < 350 °C) was associated with the formation of primary pyrite-546 chalcopyrite, or that high-temperature chloritization (350 to 250 °C) was associated with 547 bornite-chalcocite. Moreover, the Fetot/Fetot+Mg atomic ratios of Fe-clinochlore to Mg-548 chamosite suggest that fluids altered the pyroxene or residual material with the addition of 549 external Fe compared to smectite precipitation. The high Fetot/Fetot+Mg atomic ratios and high Fe²⁺/Fe³⁺ atomic ratios of these chlorites suggest an Fe–rich and reduced fluid in 550 551 agreement with the migration of Fe, Cu and S species producing sulfides. However, the 552 origin of fluid, whether the mixing of magmatic and meteoric fluids or basinal brines 553 (IOCG, Chilean 'Manto type'), was not identified. Nevertheless, the chloritization process 554 occurred from 312 to 120 °C. Despite the errors related to chlorite thermometers, the ranges

- of temperatures in the lapilli tuff (275 to 129 °C; median= 183 ± 39 °C) and andesitic dikes
- 556 (312 to 172 °C, median= 251 ± 56 °C) suggest the existence of changing thermal gradients
- 557 related to the cooling of the lava pile or intrusive dike and fluids with different
- 558 temperatures at different times.

559 The lowest-temperature stage was related to the widespread formation of Mg-560 saponite and smectite-rich C/S (200 to 50 °C). The formations of chlorites, 561 chlorite/smectite mixed-layers and Mg-saponite were related to the influx of fluids 562 (meteoric water or basinal brine) at lower thermal fluxes associated with the sulfide 563 assemblage of bornite-chalcocite, chalcocite, and barite with the increasing concentration 564 of sulfate. Consequently, the petrographic association of albite and chlorite with pyrite and 565 chalcopyrite suggests that the albitization to chloritization stage and structural control may 566 be prospective guides for Cu fertile magmatic systems. The chlorite/smectite mixed-layers emphasized favorable Cu-enriched zones, such as fluid circulation in faults or along dikes 567

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568

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and percolation in the porosity of the lapilli tuff.

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849 Figures and Tables Legends

850

851 (modified from Hartmann et al., 2007); B) Central-western Camaquã Basin geological map 852 with Seival Mine area and Cu occurrences localization (modified from Toniolo et al., 2007; 853 Gastal et al., 2015). Keys: 1= Seival Mine (Cu and Ag); 2= Silveira Mine (Cu); 3= Crespos 854 Mine (Cu); 4= Volta Grande and Merita Mine (Cu and Au). 855 856 Figure 2. Geological map of the Seival Mine. Sequence of lapilli tuff, and esitic lava flows 857 and volcanic agglomerate with andesitic and trachyandesitic dike (NE direction) from 858 Hilário Formation (HF), polymictic conglomerate and vesicular lava flows from Santa Fé 859 Formation (SFF), rhyolite dikes of Acampamento Velho Formation (AVF), faults, 860 mineralization projections, inactive open pit mines and bore-hole localization (modified 861 from Reischl, 1978; Lopes et al., 2014). Keys: 1= Barita Mine; 2= João Dahne Mine; 3= 862 Morcego Mine; 4= Meio Mine; 5= Cruzeta Mine; 6= Alcides Mine. 863 864 Figure 3. Mineralization in the Seival Mine area. A) Cu soil anomaly (modified from 865 Reischl, 1978) and inactive open pit mines, faults and Cu-mineralization; B) Schematic 866 section of alteration zones in Hilário Formation. Keys: Chl= Chlorite; C/S= 867 Chlorite/smectite mixed-layer; Hem= Hematite; Tit= Titanite; Cal= Calcite; Qtz= Quartz; 868 Cc= Chalcocite; Bn= Bornite; Smec= Smectite. 869 870 Figure 4. Macroscopic photograph (A and B), photomicrograph in natural (C and F) and 871 polarized light (D, E, G and H). A) Hand sample containing altered pyroclasts of lapilli tuff; 872 B) Hand sample with plagioclase and altered groundmass in andesite dike; C) Pervasive 873 clay minerals alteration in lapilli tuff; D) Zoned phenocryst of plagioclase with indication 874 of unaltered andesine-labradorite and altered plagioclase with albite composition in 875 andesitic dike; E) Clinopyroxene and vesicle fulfilled by smectite-rich chlorite/smectite in 876 less altered amygdaloidal andesitic lava flows; F) Amygdaloidal andesitic lava flows 877 pyroclast of lapilli tuff fulfilled by chlorite, calcite, sulfide, titanite and quartz; G) Smectite 878 in less altered andesitic lava flows; H) Vesicle fulfilled by chlorite/smectite mixed-layers in 879 andesitic lava flows. Keys: Pl= Plagioclase; Sul= Sulfide; Cal= Calcite; Tit= Titanite;

Figure 1. Geological setting of the study area. A) Schematic Sul-rio-grandense Shield map

- Hem= Hematite; Qtz= Quartz; K-fds= K-feldspar; And-lab= Andesine-labradorite; Ab=
 Albite; C/S= Chlorite/smectite mixed-layer; Px= Pyroxene; Chl= Chlorite, Smec=
- 882 Smectite.
- 883
- Figure 5. Plots of mineral compositions. A) Ca–Mg–Fe clinopyroxenes showing augite
 compositions in andesitic lava flows and andesitic dike; B) Biotite (white point) and less
 pristine biotite (gray point) in the Al_{tot} vs Al^{VI} diagram; C) Al+Fe³⁺ vs Ti and Al vs Fe binary
 diagram of the hydrothermal titanite compositions (diagram extracted from Cao et al.,
 2015); D) An–Ab–Or ternary feldspar diagram showing albitization in andesine–labradorite
 and rims with K–feldspar in some zoned plagioclase (An= Anorthite; Ab= Albite; Or=
 Orthoclase).
- 891

Figure 6. Chemical compositions of a series of saponite, chlorite and chlorite/smectite
mixed–layers in projection M⁺, 4Si and 3R²⁺ (Velde, 1985; adapted from Inoue et al., 1984)
with detail showing the smectite, chlorite–rich chlorite–smectite mixed–layer (C/S) and
chlorite compositions from Seival Mine, as well as comparison between chlorites analyzes
from epithermal Lavras do Sul (Mexias et al., 1990b, c; Bongiolo et al., 2011) and
Camaquã Mine (Renac et al., 2014).

898

Figure 7. Atomic proportions of chlorites in vein and groundmass of andesitic dikes
presented in Wiewiora and Weiss diagram (1990), of Si and divalent transition metals
normalized to chlorite atom per formula (28 oxygen total anions atoms) in comparison with
epithermal system from Lavras do Sul (Mexias et al., 1990b; Bongiolo et al., 2011) and
Camaquã Mine (Renac et al., 2014) and graphical representation of low-temperature
chlorite geothermometry (Bourdelle and Cathelineau, 2015).

905

Figure 8. X-ray diffraction patters of < 0.4 μm clay-size fraction of chlorite (A), corrensite
(B), smectite (C) and chlorite/smectite (C/S) mixed-layer (D). Keys: Air dried (black line);
EG= Ethylene glycol solvation (gray line); Heating treatment (light gray line); Chl=

- 909 Chlorite; Smec= Smectite.
- 910

911 Figure 9. S.E.M. images obtained from drill hole fresh rock sample fragment of

912 amygdaloidal andesitic lava flows described by Fontana et al. (2017). A) Albite fragment

913 associated with corrensite clay minerals of the andesitic lava flows groundmass; B) Detail

- 914 of corrensite morphology of the altered andesitic lava flows groundmass. Keys: Ab= Albite;
- 915 Cor= Corrensite.
- 916

Figure 10. REE normalized patterns by the chondrite values (McDonough and Sun, 1995).
A) Andesine–labradorite with slight albitization of group I; B) Albite–rich plagioclases of
group II.

920

Table 1. Summary of mineral, host rock and structural formula of magmatic, magmatic to
late-magmatic and hydrothermal phases. Nomenclature of chlorites after Bayliss (1975).

923

924 Table 2. Measured REE analyzes and normalized values to McDonough and Sun (1995) in 925 separate plagioclase grains of the Seival Mine, and esitic lava flows located outside of the 926 area (black line) and whole-rock analyzes (Lopes et al., 2014). Keys: And= Andesitic lava 927 flows; AD= Andesitic dike; Outs. area= Andesitic lava flows located of outside studied 928 area; Light REE= La to Sm; Heavy REE= Eu to Lu; Σ REE= Sum of total concentration of 929 not normalized rare earth elements; Eu*= The value of the Eu anomaly calculated by the formula $[Eu^*] = [((Eu_N)/(Sm_N \times Gd_N)^{1/2})]$ from Worrall and Pearson (2001) or $[Eu^*] =$ 930 931 $[((Eu_N)/(Sm_N^2 \times Tb_N)^{1/3})]$ from Lawrence and Kamber (2006). 932 933 **Supplementary Table.** Representative compositions of pyroxene (A), biotite (B), titanite 934 (C), feldspar (D) and clay minerals as chlorite (E), smectite (F) and chlorite/smectite

935 mixed–layer (G) analyzes and structural formula. Chlorite temperatures values are showed

in Supplementary Table E (Inoue et al., 2009; Bourdelle and Cathelineau, 2015).





- Santa Bárbara Group (574–544 Ma)
- Acampamento Velho Formation
 - Rhyolite dike
 - Santa Fé Formation
 - ···· Polimitic conglomerate
 - v_v^v Vesicular lava flows

- Hilário Formation
 - ✓ Trachyandesite dike
 - 🥒 Andesite dike
 - Volcanic agglomerate
 - Andesitic lava flow
 - Lapilli tuff

- Faults
- Main faults
- Mineralization
- --' River
 - レ Dipping (S0)

- Inactive mine
- 1 Barita
- João Dahne
- 3 Morcego
- 4 Meio
- 5 Cruzeta
- 6 Alcides









3R²⁺









Host rock	Mineral	Structural formula
Magmatic phase		
Andesitic lava flow and dike: less altered	Augite	$[(Ca_{0.70-0.81} Na_{0.01-0.03}) (Fe^{+2}_{0.15-0.32} Mg_{0.86-0.97}) (Al_{0.06-0.19} Ti_{0-0.02} Fe^{+3}_{0-0.06}) (Si_{1.88-1.99}) O_{12}]$
Trachyandesitic dike: magmatic or pristine	Mg-biotite	[(Ca 0.01-0.03 Na 0.09-0.25 K 0.61-1.41) (Fe ⁺² 1.92-2.3 Mg 2.95-3.81 Mn 0.01-0.03 Al 0-0.07 Ti 0.44-0.76) ^{VI} (Al 2.61-2.98
Trachyandesitic dike: less pristine	Mg-biotite	[(Ca 0.01-0.02 Na 0.20-0.24 K 1.22-1.49) (Fe ⁺² 1.79-2.02 Mg 2.72-2.89 Mn 0.01-0.02 Al 0.07-0.33 Ti 0.61-0.75) ^{VI} (Al 2.39-2
Magmatic to late-magmatic phase		
Andesitic dike: euchdral to agglomerates	Titanite	$[(Ca_{0.94-1.02} \square_{0.02} Ti_{0.79-0.88} Al_{0.09-0.16} Fe^{3+}_{0.03-0.09} Mg_{0-0.03} Si_{1.01-1.07} O_5)]$
Andesitic dike and lava flow: less altered	Andesine-labradorite	[(An _{0.43-0.53} Ab _{0.43-0.54} Or _{0.03-0.05})]
Andesitic dike	K–feldspar	[(An _{0.43-0.53} Ab _{0.43-0.54} Or _{0.03-0.05})]
Andesitic lava flow and dike: more altered	Albite	[(An _{0-0.06} Ab _{0.89-1} Or _{0-0.10})]
Hydrothermal phase		
* Porphyritic andesitic lava flow: augite replacement	Mg-chamosite to Fe-clinochlore	$[(Ca_{0.04-0.06} Na_{0-0.04} K_{0.02-011}) (Al_{2.70-3.03} Ti_{0-0.01} Fe^{3+}_{0.37-0.57} Fe^{2+}_{3.61-5.23} Mg_{3.07-3.97} Mn_{0.01-0.04})^{VI} (Se^{3+}_{0.01-0.01} Fe^{3+}_{0.01-0.01} Fe^{3+}_{0.01-$
** Lapilli tuff: filled vugs	Mg-chamosite	$[(Ca_{0-0.03} Na_{0-0.04} K_{0-0.11}) (Al_{2.70-3.11} Ti_{0-0.01} Fe^{3+} _{0.31-0.46} Fe^{2+} _{4.38-5.14} Mg_{3.17-3.50} Mn_{0.01-0.02})^{VI} (Si_{5.00} K_{0-0.01} K_{0-0.01})^{VI} (Si_{5.00} K_{0-0.01} K_{0-0.01} K_{0-0.01} K_{0-0.01})^{VI} (Si_{5.00} K_{0-0.01} K_{0-0.01} K_{0-0.01} K_{0-0.01})^{VI} (Si_{5.00} K_{0-0.01} K_{0$
*** Andesitic dikes: matrix	Mg-chamosite to Fe-clinochlore	$\left[\left(Ca_{0.03-0.12} Na_{0-0.03} K_{0.01-0.05}\right) \left(Al_{1.63-2.13} Ti_{0-0.01} Fe^{3+} _{0.1-0.28} Fe^{2+} _{4.26-5.49} Mg_{4.4-4.74} Mn_{0.03-0.08}\right)^{VI} \left(OH^{10} Re^{3+} _{0.1-0.28} Fe^{3+} _{0.1-0.28} F$
Amygdaloidal andesitic lava flow: less altered rocks	Mg-saponite	$[(Ca_{0.18-0.31} Na_{0.02-0.05} K_{0.02-0.07}) (Al_{0.06-0.23} Ti_{0-0.01} Fe^{+2}_{1.35-1.78} Mg_{4.50-4.81} Mn_{0.02-0.03})^{VI} (Si_{6.41-6.98} Mn_{0.02-0$
Amygdaloidal andesitic lava flow: less altered rocks	Chl-rich C/S mixed-layer	$[(Ca_{0.05-0.16} Na_{0-0.09} K_{0.01-0.05}) (Al_{1.59-1.93} Ti_{0-0.01} Fe^{3+} _{0.18-0.49} Fe^{2+} _{2.68-3.77} Mg_{5.70-6.37} Mn_{0.03-0.05})^{V}$
Porphyritic andesitic lava flow: more altered rock	Chl-rich C/S mixed-layer	$[(Ca_{0.05-0.07} Na_{0.02-0.06} K_{0.01-0.03}) (Al_{2.21-2.46} Ti_{0-0.02} Fe^{3+}_{0.46-0.61} Fe^{2+}_{2.19-2.74} Mg_{5.59-5.86} Mn_{0.06-0.07})^{VI}$

 $(Si_{5.94-6.24} Al_{1.76-2.06})^{IV} O_{20} (OH)_{8}]$ 5.62-6.01 Al $_{1.99-2.38})^{IV} O_{20} (OH)_{8}]$ OH)₄ (Si $_{6.20-6.62} Al_{1.38-1.80})^{IV} O_{20} (OH)_{8}]$ OH)₄ (Si $_{6.20-6.62} Al_{1.38-1.80})^{IV} O_{20} (OH)_{8}]]$ OH)₄ (Si $_{6.53-7.23} Al_{0.77-1.47})^{IV} O_{20} (OH)_{8}]$ VI (Si $_{6.52-6.75} Al_{1.25-1.48})^{IV} O_{20} (OH)_{8}]$

Sample (mg/kg)	FM 13	DD 62	RFM 66	RFM 55	WL 13	WL 19	FM 33	FM 32	DD 76	RFM 68
	Group I			Group II						Outs. Area
	AD	AD	AD	And	And	And	AD	AD	AD	And
Y	0.23	1.61	1.63	9.18	3.15	2.26	0.41	1.36	11.03	1.24
La	1.66	6.18	9.95	28.39	7.70	5.47	2.16	4.30	31.66	8.09
Ce	2.68	15.41	17.54	55.31	19.25	16.08	5.57	14.19	60.18	13.61
Pr	0.32	1.65	1.90	8.15	2.29	2.06	0.66	1.89	7.79	1.46
Nd	1.14	6.10	6.54	32.46	8.71	8.07	2.51	7.31	29.43	5.04
Sm	0.18	1.77	1.51	5.85	2.12	2.25	0.45	2.61	6.47	0.82
Eu	0.17	1.79	2.36	2.28	0.60	0.67	0.17	0.82	3.05	1.75
Gd	0.18	1.89	1.62	5.55	1.94	1.92	0.37	2.19	6.50	0.90
Tb	0.02	0.21	0.17	0.74	0.26	0.26	0.04	0.28	0.81	0.09
Dy	0.07	0.78	0.58	3.07	1.11	1.05	0.16	1.04	3.20	0.30
Но	0.02	0.15	0.11	0.65	0.23	0.21	0.03	0.20	0.63	0.06
Er	0.04	0.40	0.31	1.80	0.59	0.56	0.09	0.54	1.64	0.16
Tm	0.01	0.06	0.04	0.28	0.09	0.09	0.01	0.08	0.24	0.02
Yb	0.03	0.29	0.22	1.46	0.45	0.45	0.07	0.39	1.21	0.11
Lu	0.01	0.08	0.05	0.35	0.12	0.12	0.02	0.12	0.29	0.03
Normalization standard CI chondrite (McDe	onough and S	Sun, 1995)								
La _N	6.99	26.07	42.00	119.77	32.50	23.10	9.10	18.16	133.6	34.12
Ce _N	4.37	25.14	28.62	90.23	31.40	26.23	9.09	23.15	98.18	22.21
Pr _N	3.41	17.80	20.48	87.81	24.68	22.19	7.12	20.42	83.91	15.70
Nd _N	2.49	13.35	14.32	71.04	19.06	17.66	5.48	16.01	64.4	11.03
Sm _N	1.20	11.98	10.22	39.55	14.32	15.20	3.02	17.66	43.73	5.53
Eu _N	3.04	31.85	41.95	40.48	10.57	11.87	2.98	14.55	54.09	31.07
Gd _N	0.89	9.50	8.14	27.90	9.74	9.66	1.88	10.98	32.67	4.50
Tb _N	0.55	5.73	4.63	20.44	7.31	7.15	1.22	7.73	22.49	2.41
Dy _N	0.30	3.16	2.35	12.48	4.50	4.26	0.64	4.24	13.02	1.21
Ho _N	0.27	2.71	2.03	11.83	4.12	3.83	0.57	3.70	11.45	1.04
Er _N	0.26	2.51	1.94	11.27	3.69	3.53	0.56	3.39	10.26	0.98
Yb _N	0.20	1.82	1.37	9.09	2.80	2.81	0.43	2.43	7.54	0.69
Lu _N	0.28	3.09	2.15	14.27	4.72	4.88	0.69	4.67	11.91	1.06
ΣLREE	5.98	31.11	37.44	130.16	40.07	33.93	11.35	30.30	135.53	29.02
ΣHREE	0.55	5.65	5.46	16.18	5.39	5.33	0.96	5.66	17.57	3.42
ΣREE	6.76	38.37	44.53	155.52	48.61	41.52	12.72	37.32	164.13	33.68
$[Eu^*] = [((Eu_N)/(Sm_N \times Gd_N)^{1/2})]$	1.22	0.90	0.98	2.94	2.99	4.60	1.25	1.04	1.43	6.23
$[Eu^*] = [((Eu_N)/(Sm_N^2 \times Tb_N)^{1/3})]$	1.28	0.92	1	3.29	3.40	5.35	1.33	1.09	1.54	7.41