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# <sup>30</sup> <sup>40</sup>Ar-<sup>39</sup>Ar age of the copper mineralization at Riacho do Pontal IOCG

31 **District and detrital zircon U–Pb ages of paragneiss host rocks** 

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# 49 ABSTRACT

50 Geological, structural and metallogenetic characteristics related to the Proterozoic

51 Riacho do Pontal iron-oxide copper gold (IOCG) mineral systems in northeast Brazil

- 52 have been reinterpreted recently and there is an ongoing discussion regarding their
- genetic model and associated tectonic setting. The mineralization in the Riacho do
   Pontal district is represented by small copper deposits strongly controlled by the
- Pontal district is represented by small copper deposits strongly controlled by the
   structural features of the basement rocks. Hydrothermal biotite associated to the copper
- 56 mineralization has a  ${}^{40}$ Ar- ${}^{39}$ Ar of ca. 691 Ma, indicating a probable late Neoproterozoic
- 57 age for the main mineralization event. Detrital zircon grains from the host rock show
- 58 that the sedimentary protolith is younger than ca. 2035 Ma and was probably deposited
- in a convergent setting, representing a favorable environment for the formation of Cu-
- 60 rich porphyry. Our results thus help to link the tectonic setting of the Riacho do Pontal
- 61 Belt to its copper-gold ore deposits.
- 62
- 63 **Keywords:** Riacho do Pontal District, IOCG, <sup>40</sup>Ar-<sup>39</sup>Ar ages, Detrital zircon.
- 64

# 65 **1. INTRODUCTION**

- 66 The São Francisco Craton, located in southeast Brazil, represents one of the main
- 67 cratonic area in South America (Fig. 1A)(Alkmim and Marshak, 1998; Cordani et al.,
- 68 2016; Lana et al., 2013; Romano et al., 2013; Teixeira and Figueiredo, 1991). The São

69 Francisco Craton comprises three main continental blocks that stabilized by the end of 70 the Archean, referred to as the Gavião, Jequié and Serrinha blocks, and magmatic arcs of 71 the Itabuna-Salvador-Curaça Belt (Fig. 1B) (Barbosa and Barbosa, 2017). These blocks 72 and continental arcs were amalgamated together during the early Paleoproterozoic as a result of the Transamazonian Orogeny (Almeida et al., 2000; Baldim and Oliveira, 2021; 73 74 Barbosa and Barbosa, 2017; Barbosa and Sabaté, 2004; Hurley et al., 1967; Teixeira and 75 Figueiredo, 1991; Zincone et al., 2021). Remnants of the Transamazonian Orogen 76 located at the border of the São Francisco Craton were later reworked and overprinted 77 by the Brasiliano/Panafrican Orogeny, which resulted in the formation of numerous 78 orogenic belts surrounding the São Francisco Craton, among which the Riacho do Pontal 79 Belt represents an important, although yet poorly documented segment of this orogenic 80 system. Brasiliano/Panafrican belts resulted from the formation of the supercontinent 81 Gondwana at the end of the Neoproterozoic and beginning of the Paleozoic (Aguilar et 82 al., 2017; Bertrand and Jardim de Sa, 1990; Caxito et al., 2016; Cutts et al., 2019, 2018; 83 Heilbron et al., 2010; Moreira et al., 2018; Narduzzi et al., 2017; Schannor et al., 2019).

84 The Riacho do Pontal Belt, located in to the north of the of the Gavião Block is a 85 part of the giant strike-slip system of the Borborema Province (Fig. 1) (Barbosa and Barbosa, 2017; Caxito et al., 2014a; Heilbron et al., 2017). Like other Archean and 86 87 Precambrian terranes within and bordering the São Francisco Craton, such as the 88 Quadrilátero Ferrífero (Farina et al., 2016), the Riacho do Pontal Belt comprises zones 89 with significant mineral resources forming ore deposits referred to as the Riacho do 90 Pontal Mineral District. The latter is situated in the southern portion of Borborema 91 Province (Fig. 1) and consists of a cupriferous province subdivided in two districts: the 92 Vale do Curaçá and the Riacho do Pontal copper districts (Garcia, 2017). The province 93 also comprises mineralization in Au, Fe and Cr and other metals (Teixeira et al. 2010, 94 2019; Juliani et al. 2016). The relationships between copper ore deposits and the 95 geodynamic evolution of the region are debated. This is partly due to the complex, yet 96 incompletely understood geodynamic evolution of this area, which experienced at least 97 two orogenic cycles which could have both contributed to ore mineralization. Garcia 98 (2017) emphasized that ore deposits mainly formed during the Neoproterozoic 99 Brasiliano/Panafrican orogenic cycle. In detail, Garcia (2017) suggested that 100 Neoarchean (ultra)mafic magmatic rocks constitute the main copper source that was 101 later remobilized by hydrothermal processes during the Brasiliano/Panafrican Orogeny. 102 On the contrary, gold mineralization is suggested to have occurred during the 103 Transamanzonian Orogeny, with some remobilization and mineralization events during 104 the Brasiliano/Panafrican Orogeny (Teixeira et al., 2019). Alternatively, Hühn et al. 105 (2020) pointed out that the Vale do Curaçá and the Riacho do Pontal copper districts are 106 located within the northern part of the São Francisco Craton and represent two pulses of 107 mineralization (Fig. 2). An older magmatic event associated with the Caraíba Cu deposit, 108 which is located within the Vale do Curacá District, is related to Paleoproterozoic (ca. 2.0 109 to 2.2 Ga) hydrothermal processes. A younger Neoproterozoic (ca. 630 Ma to 530 Ma) episode of volcanism and associated plutonism is also documented in the Riacho do 110 111 Pontal Belt (Caxito et al., 2017).

112 The main objective of this study is to document the ages of mineralizing events of 113 copper deposits in the Riacho do Pontal Mineral District and their link with the 114 geodynamic evolution of the Riacho do Pontal Belt. To this purpose, we provide new 115 geochronological <sup>40</sup>Ar-<sup>39</sup>Ar age obtained on hydrothermal biotite and U-Pb ages 116 obtained on zircon from the host rocks. Based on these data, we propose a model for the 117 Cu mineralization of the Riacho do Pontal Mineral District. 118

# 119 2. GEOLOGICAL SETTING

#### 120 2.1. Regional setting

The northern part of the São Francisco Craton is bordered, from west to east, by the Rio
Preto, the Riacho do Pontal and the Segipano belts (Fig. 1B). These belts corresponds to
segments of the Brasiliano/Panafrican collisional zone that resulted from the
convergence between Borborema Province and the São Francisco Craton between ca.
640 Ma to ca. 500 Ma (Alkmim and Martins-Neto, 2012; Caxito et al., 2017; Heilbron et
al., 2017).

Within the Riacho do Pontal Belts, a suture zone is marked by a negative-positive pair of strong gravimetric anomalies. The positive anomaly corresponds to the lower crust of the Borborema Province, and the negative signal corresponds to nappes pushed towards the craton (Oliveira, 2008). The supracrustal rocks of the Riacho do Pontal and Sergipano belts crop out as allochthon, with displacements of the order of 30 to 60 km over the São Francisco Craton (Jardim de Sá et al. 1992; Oliveira, 2008).

133 The Borborema Province records deformation and magmatism related to the 134 Brasiliano Orogeny and comprises domains of distinct evolution juxtaposed by shear zones (Jardim de Sá et al., 1992; Jardim de Sá, 1994; (Caxito et al., 2016, 2014a). The 135 136 main lithostratigraphic terranes of the Borborema Province were formed or metamorphosed during the early Neoproterozoic Cariris Velhos Orogeny (ca. 1000 Ma 137 to 960 Ma; (Caxito et al., 2014b) and the Late Neoproterozoic Brasiliano/Panafican 138 139 Orogeny (ca. 630 Ma to 530 Ma; Santos, 1996; (Caxito et al., 2016, 2014a). The 140 Borborema Province is classically subdivided into five major tectonic blocks: 1) Médio 141 Coreaú; 2) Ceará (or Cearense); 3) Rio Grande do Norte; 4) Transversal Zone or Central: 142 and 5) South or External (e.g., Santos et al. 1997; Brito-Neves et al., 2000; Oliveira and Medeiros, 2000; Oliveira, 2008). The contact of the Borborema Province with the 143 144 northern portion of the São Francisco Craton is represented by the fronts of the 145 Brasiliano Nappes. This area corresponds to the Brasiliano collisional zone that resulted 146 from a tangential tectonic event with a transpressive component and mass transport 147 towards the São Francisco Craton (Alkmin et al., 1993). According to Oliveira (2008), 148 this region shows an aeromagnetic pattern characterized by dominantly shallow 149 sources, defined by positive linear axes oriented towards E-W, with amplitude lower 150 than 100 nT and short wavelength (10 km), intercalated with negative linear and 151 ellipsoidal anomalies.

152

# 153 **2.2. Local geology of Riacho do Pontal Belt**

The Riacho do Pontal Belt is located in the southern portion of the Borborema Province (Brito-Neves 1975, 1983; Almeida et al. 1976; (Almeida et al., 2000) (Figs. 1 and 3). From south to north, the Riacho do Pontal Belt is subdivided into the External, Central and Internal zones which are characterized by distinct sedimentary, metamorphic and structural features (Caxito et al., 2016). The External Zone comprises south-verging nappes overriding the São Francisco Craton basement. The Central Zone is made up of metavolcaniclastic rocks deformed by south-verging thrusts and E–W strike -slip faults. The Central zone also comprises rock units interpreted as Neoproterozoic ophiolites
(Caxito et al., 2016, 2014a). The Internal Zone comprises metavolcaniclastic, gneiss and
migmatites (Caxito et al., 2016).

164 The Riacho do Pontal Mineral District was the focus of intense exploration from 165 the seventies to the nineties, during the mineral exploration boom. Efforts were mainly 166 focused on the characterization Volcanic-Hosted Massive Sulfide mineralization in 167 greenstone belts (VHMS; Franklin et al., 1981; Barrie and Hannington, 1999) and copper mineralization in mafic-ultramafic layered complexes. Several copper occurrences have 168 169 been recognized during this period (Delgado and Sousa, 1975) and have been 170 considered as VMS type (CBPM 2001). The possibility that copper deposits could be 171 associated with iron oxides, similar to Iron Oxide Copper-Gold deposits know elsewhere 172 (IOCG deposits; Hitzman et al. 1992; Hitzman 2000), was emphasized only in more 173 recent studies (Maas et al., 2003; Hühn et al., 2011). Early investigations conducted by 174 the Companhia Baiana de Pesquisa Mineral (CBPM) near the Riacho Seco town (Fig. 3) 175 showed that these deposits are located along a WNW shear zone and hosted in biotite-176 garnet mylonites, revealing important structural control. Mineral assessment conducted 177 by CBPM indicates a reserve of 5 Mt @ 0.8% Cu for this deposit.

178 Since then, more than twenty copper occurrences have been described in the 179 Riacho do Pontal Mineral District, among which the Ria4 and the Riacho Seco deposits 180 are the main Cu occurrences (Fig. 2; Teixeira et al., 2010). Geologically, these 181 occurrences are mostly located in the contact zone between the Borborema Province and the São Francisco Craton. Copper occurrences are structurally controlled by shear 182 zones similar to those reported in other areas of the Borborema Province (Parente et al., 183 184 2004, Caxito et al., 2014a, Hühn et al., 2011; 2018, Garcia 2017). In addition to tectonic structures, hydrothermal processes have been shown to control ore mineralization and 185 several alteration types related to hydrothermal processes have been identified in the 186 187 Riacho do Pontal District (Hühn et al. 2014).

188

# 189 **3. METHODOLOGY**

#### 190 **3.1. Sampling, samples and characterization of hydrothermal overprint**

191 Sampling has been conducted in three cored wells (RIA4-DH00001-001, RIA4-

192 DH00001-003 and RIA4-DH00002) drilled where the RIA4 malachite occurrence hosted

193 in folded biotite-rich rocks has been documented (Fig. 3). Drill core location and

sampling depth are provided in the Appendix A. The samples consist of paragneisses and

- 195 migmatites which have been overprinted by hydrothermal alteration. To further
- document hydrothermal alteration, we conducted petrographic studies using Energy-
- 197 Dispersive X-ray spectroscopy (EDX), which allows characterizing hydrothermal mineral
- signatures (Hühn et al., 2014; Hühn et al., 2018). To complement EDX analyses, Electron
- 199 Microprobe Analyses (EMA) have been conducted for precise determination of the 200 composition of biotite minerals related to hydrothermal processes.
- 200

# 202 **3.2.** Whole rocks elemental geochemical analyses

All samples were digested by Agua Regia and analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for major and trace element analyses (33 analyzed
 elements). The elemental geochemical data were then used to select samples for further
 geochronological analyses.

207

# 208 **3.3.** <sup>40</sup>Ar-<sup>39</sup>Ar geochronology

One biotite sample has been dated and was loaded into a 21-pits aluminum disk along
with the neutron fluence monitor Fish Canyon Sanidine (age 28.201 ± 0.046 Ma),
following the geometry illustrated in Vasconcelos et al. (2002). The irradiation disks
were closed with aluminum covers, wrapped in aluminum foil and vacuum heat sealed
into quartz vials. All samples were irradiated for 14 hours over the period from 8 June
2016 to 10 June 2016 in the Cadmium-lined B-1 CLICIT facility, a TRIGA-type reactor,
Oregon State University, USA.

216 After irradiation, noble gas mass spectrometry was performed in a fully automated MAP-215–50 mass spectrometer equipped with a Balzers 217 electron 217 multiplier. The heating time for all analyses was  $\sim$ 45 seconds, not including the laser 218 219 ramp-up time. The error in the I factor is not included in the tabulated error in the age in 220 Appendix B, but is included in all plateau ages throughout the text. The mass 221 spectrometer gain was calculated based on the analysis of an air pipette  $(1.634 \times 10^{-13})$ 222 moles <sup>40</sup>Ar) on the Faraday detector (4.257 mV) equipped with a 1 x 10<sup>11</sup> Ohms resistor, vielding a Faraday sensitivity of 3.84 x 10<sup>-9</sup> moles/nA. The current multiplier sensitivity 223 measured on a Balzers 217 Electron Multiplier, operated with a gain of ~145,000 is ~4.5 224 225 x 10<sup>-14</sup> moles/nA. The historical irradiation correction factors for the CLICIT facility, 226 TRIGA reactor, Oregon State University, USA are: (2.64 ± 0.02) x 10<sup>-4</sup> for (<sup>36</sup>Ar/<sup>37</sup>Ar) Ca, 227  $(7.04 \pm 0.06) \times 10^{-4}$  for  $({}^{39}\text{Ar}/{}^{37}\text{Ar})$  Ca, and  $(8 \pm 3) \times 10^{-4}$  for  $({}^{40}\text{Ar}/{}^{39}\text{Ar})$  K (values determined at the Berkeley Geochronology Center; Appendix B). Age plateaus were 228 229 defined as at least three consecutive steps yielding apparent ages within  $2\sigma$  error from the variance-weighted mean, comprising 50% or more of total <sup>39</sup>Ar released (Fleck et al., 230 231 1977). Plateau age errors are reported at the 95% confidence level  $(2\sigma)$  and include the 232 errors in the irradiation correction factors and the error in J, but do not include the 233 uncertainty in the potassium decay constants.

234

# 235 **3.4. U-Pb zircon geochronology**

#### 236 3.4.1. Analytical methods

237 Zircon U-Pb ages were obtained using the Sensitive High-Resolution Ion Microprobe -238 Reverse Geometry (SHRIMP-RG) at the Research School of Earth Sciences (RSES), The 239 Australian National University (ANU). following the procedures described by Williams (1998) and Ireland et al. (2008). Briefly, a 2–4 nA mass filtered  $O_2^-$  primary ion beam 240 241 was focused to a spot ca. 25 µm diameter, positive secondary ions were extracted at 10 kV. The magnet was stepped through peaks of  ${}^{90}$ Zr $_{2}{}^{16}$ O,  ${}^{204}$ Pb,  ${}^{206}$ Pb,  ${}^{207}$ Pb,  ${}^{208}$ Pb,  ${}^{238}$ U, 242 <sup>232</sup>Th<sup>16</sup>O, and <sup>238</sup>U<sup>16</sup>O. FC1 zircon standard (Paces and Miller Jr., 1993; 1099 ± 0.5 Ma) 243 was used for <sup>206</sup>Pb/<sup>238</sup>U calibration, whereas the OGC zircon (Stern et al., 2009; 3465.4 ± 244 0.6 Ma) was used for <sup>207</sup>Pb/<sup>206</sup>Pb calibration and to monitor instrument-induced mass 245

- fractionation he common Pb correction was based on the measured <sup>204</sup>Pb/<sup>206</sup>Pb
  (Compston et al., 1984). Data reduction and plotting were processed with SQUID 2
  (Ludwig, 2009) and IsoplotR (Vermeesch, 2018), respectively.
- 249

#### 250 *3.4.2. Data filtering and age calculations*

251 As zircon grains were collected in high-grade metasedimentary rocks, a special attention 252 was paid to zircon microstructures identified by cathodoluminescence (CL) imaging. Maximum depositional ages (MDA) were calculated from analyses performed in the 253 254 cores of zircon grains, avoiding rims and overgrowths that could have crystalized during high-grade metamorphism and rims that could have suffered Pb loss. After selecting 255 256 analyses performed in zircon cores, a two-step procedure has been applied to calculate 257 MDAs. The first step consisted of filtering the data based on their probability of 258 concordance calculated using IsoplotR (Vermeesch, 2018), including decay constant 259 errors. The cut-off level applied to filter the data was 10% (Rossignol et al., 2016). As 260 slight Pb loss could still result in apparently concordant dates, resolving whether the 261 data represent truly concordant ages or apparently concordant dates requires a close 262 inspection of each dataset (Corfu, 2013). In cases where the data do not show evidence 263 of Pb loss, with no skewed age distribution toward younger ages (Spencer et al., 2016), 264 MDAs were calculated for each sample from the youngest cluster of at least three grains 265 overlapping at  $2\sigma$  (standard deviation) (Coutts et al., 2019; Dickinson and Gehrels, 266 2009) as the concordia age of these youngest clusters (Ludwig, 1998). In cases where data show skewed distribution toward younger ages, the selection of data to calculate a 267 268 weighted mean concordia date from multiple analyses is discussed in detail in the text, 269 because such spreading could result from variable amounts of Pb loss, hence producing 270 apparently concordant dates with no geological significance.

The age of metamorphic events was calculated as the lower intercept of the unforced discordia passing through analyses that align along a Pb loss trend in the Wetherill diagram. To regress the data for intercept date calculations, the points were weighted proportionally to the inverse square of their errors ("model 1" regression in IsoplotR; Vermeesch, 2018). All uncertainties are provided with 95% confidence limits.

#### 277 3.4.3. Analyses of age distributions

To assess the tectonic setting of deposition of the studied sedimentary unit, we used the 10<sup>th</sup>-50<sup>th</sup> percentile age difference in age distribution combined with a modified  $\chi^2$ statistic distribution of the zircon population (Barham et al., 2022). The latter parameter was calculated by binning detrital zircon ages from the youngest grain age to 4 Ga. This approach is independent of the age of deposition and allow to discriminate convergent from divergent settings (Barham et al., 2022).

283 from divergent setting 284

# 285 **4. RESULTS**

# 286 4.1. Petrography and geochemistry

287 Rocks of the Riacho do Pontal prospect have a strong NW-SE lineation and were 288 overprinted by two main shearing events: a) D1-top to the north thrusting, forming a 289 series of northwest-trending parallel structures related to hydrothermal alteration and 290 mineralization; and b) D2-dextral strike-slip shear zones showing evidence of multiple 291 reactivations that are responsible for strong shearing. Both events were related to 292 transpressive structural regimes. Locally, strongly mylonitized rocks along shear zones 293 define an L-S tectonic fabric. Ore zones are strongly controlled by shear zones and 294 breccia zones along the bends of shear zones. The drill core RIA4-DH00001-001 (Fig. 2) 295 intersects paragneiss comprising malachite occurrences down to 32m, and pyrite-296 chalcopyrite-bornite down to 157m. biotite-quartz leucogneiss with quartz veins 297 parallel to the foliation and chalcopyrite as accessory mineral The drill core RIA4-298 DH00002 also intersects malachite occurrences and foliated leucogneiss with silicified 299 zones and several biotite-rich or amphibole-rich intervals, some having trace 300 chalcopyrite and pyrite. Magnetite, albite and biotite are derived from the hydrothermal 301 alteration related to shear zones.

Geochemical results from mineralized samples collected in the three drill-cores
have Cu contents up to> 10 000 ppm. The Cu content shows a moderate correlation with
Au content. Gold and copper correlate well with Fe, K, Na, Al, Ba, Co, Cr, Mg, Ni and Ti
contents.

Based on the Fe, Mg, K and Ti contents from electron microprobe analyses, biotite
minerals are classified as iron-rich biotite type (Figs. 4A and 4B; Nachit et al., 1985;
Foster, 1960; Ardalan et al., 2014). The formation of such biotite is related to
hydrothermal alteration process.

310

# 311 **4.2.**<sup>40</sup>Ar-<sup>39</sup>Ar geochronological results

The sample (PCB-R002) corresponds to biotite grains extracted from a biotite- and amphibole-rich mylonite. This sample yielded a plateau age of 691.0 ± 3.7 Ma (MSWD = 0.49; Fig. 5).

315

# 316 4.3. U-Pb geochronological results

Cathodoluminescence images of representative grains and geochronological results arepresented in Fig. 6. Analytical results are available in the Appendix C.

319

Sample DH001-003. Most of the grains appear rounded to sub-rounded (Fig. 6A) and
exhibit various sizes ranging from ca. 50 µm to ca. 200 µm, and a few grains are subangular and elongated. Most of the grains have no apparent internal structure in CL, but
some grains display a core-rim texture, with the core displaying a typical oscillatory
zoning and the rim lacking particular structure. A total of 63 spots on 63 zircon grains
were measured, among which 55 are concordant.

In a Wetherill diagram, concordant analyses spread along the concordia line between ca. 1985 Ma and ca. 2060 Ma (Fig. 7A). The age distribution of this sample is unimodal, with most of the grains being centered around ca. 2040 Ma, and skewed toward younger ages, suggesting that the youngest concordant grains suffered Pb loss (Fig. 7B). Discarding the 12 youngest grains that could have been affected by Pb loss, a
concordia date of 2034.6 ± 5.0 Ma based on 27 grains (MSWD of concordance and
equivalence = 1.4, probability of concordance and equivalence = 0.04; Fig. 7A) is
interpreted as the MDA for this sample.

334

Sample DH002-009. Zircon grains from this sample are mostly rounded to sub-rounded.
In CL, the grains show various structures. Some grains displaying a typical oscillatory
zoning, other have a core-rim texture or a patchy zonation, and some grains do not show
any particular structure (Fig. 6B). Several grains show metamitic zones.

339 A total of 35 analyses on 32 grains were measured, among which only three 340 analyses are concordant (Fig. 7C). The two youngest concordant analyses give a concordia age of  $2938.0 \pm 26.4$  Ma grains (MSWD = 2.7, probability = 0.04), but the 341 342 statistical requirements are not met to confidently consider this date as MDA. The other 343 concordant analysis gives a slightly older Mesoarchean date of 2993.1 ± 4.1 Ma. All the 344 other spot measurements suggest that the grains had undergone either significant post 345 or pre-depositional modification. Most analyses align a in a Wetheril diagram, allowing 346 to calculate an upper intercept date of 2945.0 ± 15.1 Ma and a lower intercept date of 347 584.7 ± 21.3 Ma (MSWD = 4.5; n = 25; Fig. 7C). The upper intercept is identical, within 348 uncertainties, to the concordia age calculated from the two youngest concordant grains 349 and might correspond to the age of the main detrital zircon population comprised in this 350 sample. The lower intercept could correspond to a metamorphic overgrowth or Pb-loss 351 event.

352

Sample DH001-0010. This sample yielded only a few, rather large grains (ca. 200 μm)
(Fig. 6C). In CL, a few grains display oscillatory zoning but most of the grains are
characterized by a patchy zonation typical of metamorphic zircon (Corfu et al., 2003).

Eleven analyses were performed on 11 grains, all yielding highly discordant results (Fig. 7D). Regression of all points gives an upper intercept age of 2039.9 ± 26.5 Ma and a lower intercept at 491.3 ± 29.6 Ma (MSWD = 0.54). The upper intercept is identical, within uncertainties, to the MDA of sample DH001-003 and might correspond to the age of the main detrital zircon population comprised in this sample. The lower intercept could correspond to a metamorphic overgrowth or Pb-loss event.

# 362 **5. DISCUSSION**

# 363 **5.1. Age of copper mineralization in the Riacho do Pontal District**

364 The biotite minerals comprised in the samples investigated in this study are of 365 hydrothermal origin (Fig. 4; Nachit et al., 1985; Foster 1960; Ardalan et. al., 2014). The 366  $^{40}$ Ar- $^{39}$ Ar plateau age of 691.0 ± 3.7 Ma given by a biotite sample (Fig. 5) is thus 367 interpreted as the age of the main hydrothermal event. Consequently, the Cu deposit 368 investigated here has a Neoproterozoic age. This age is older than the main collisional 369 event that formed the Riacho do Pontal Belt (Caxito et al., 2016, 2014a). The age of 370 copper mineralization could thus correspond to the initial stage of convergence of the 371 Riacho do Pontal orogenic cycle. 372

# 373 **5.2.** Ages of deposition of host-rocks and metamorphic events

374 Copper mineralization occurred in metasedimentry rocks, of which the MDA of the sample DH001-003 indicates that this sedimentary unit is younger than 2034.6 ± 5.0 Ma. 375 376 This shows that the deposition occurred during or after the late Rhyacian. The lower 377 intercepts given by samples DH002-009 and DH001-0010 suggest that the sedimentary protolith underwent one or several metamorphic event(s) at 584.7 ± 21.3 Ma and 491.3 378 ± 29.6 Ma, i.e., during the latest Neoproterozoic to Cambrian. The MDA and lower 379 380 intercept ages thus give a large time-window, ranging from the late Rhyacian to the early Cambrian, during which this sedimentary unit could have been deposited. 381

382 The latest Neoproterozoic to Cambrian metamorphic event(s) recorded by samples DH002-009 and DH001-0010 might correspond to the building of the Riacho do 383 384 Pontal Orogen, that occurred between the Ediacarian (ca. 620 Ma) and the Cambrian (ca. 385 530 Ma) as a result of the collision between the São Francisco Craton and the Borborema 386 Block (present-day coordinates; (Caxito et al., 2017, 2016). The oldest metamorphic 387 event, at 584.7 ± 21.3 Ma could record syn-collision high grade metamorphism, while 388 the younger metamorphic event at  $491.3 \pm 29.6$  is more likely related to the late 389 orogenic evolution, characterized by of large shear zones and he emplacement of late-390 orogenic plutonic rocks (Caxito et al., 2016).

391

#### 392 **5.3.** Potential provenances and tectonic setting of deposition

393 Zircon age distribution of the sedimentary units investigated in this study shows a main 394 peak around 2035 Ma and a smaller peak at ca. 2950 Ma (Fig. 8A). Zircon grains from the ca. 2035 Ma population likely derive from magmatic rocks that formed during the 395 396 Transamazonian Orogeny that resulted from the collision between the Serrinha and 397 Gavião blocks (Fig. 1B) (Baldim and Oliveira, 2021; Barbosa and Barbosa, 2017; Barbosa 398 and Sabaté, 2004; Teixeira and Figueiredo, 1991; Zincone et al., 2021). The minor 399 Mesoarchean population likely originate from magmatic rocks forming the basement of 400 the São Francisco Craton (Farina et al., 2015; Lana et al., 2013) or from the erosion of 401 sedimentary rocks containing such Mesoarchean zircon population (Rossignol et al., 402 2020). Zircon grains found in the studied sedimentary unit thus all originate from the 403 São Francisco Craton. Although based on a limited number of zircon grains, the 404 sedimentary unit investigated in this work exhibit marked differences in zircon 405 provenance with the Formosa Fm., a ca. 1.96 Ga unit of the Rio Preto Belt, located ca. 200 406 km to the southwest of the Riacho do Pontal Belt (Fig. 8B) (Caxito et al., 2014a). This 407 difference in age distribution also indicates contrasted tectonic settings during the 408 deposition of both sedimentary units (Fig. 8C). While the Formosa Fm plot in the field of 409 divergent settings, the sedimentary unit studied in this work show a marked affinity for 410 convergent settings. This suggests that the sedimentary unit investigated in this study could have been deposited in a Paleoproterozoic foreland basin associated with the 411 412 Transamazonian orogeny (Baldim and Oliveira, 2021; Barbosa and Barbosa, 2017; 413 Barbosa and Sabaté, 2004; Teixeira and Figueiredo, 1991; Zincone et al., 2021). 414 Alternatively, the sedimentary unit studied in this work could also have been deposited 415 in a convergent setting related to the building of the Riacho do Pontal Orogen during the 416 Neoproterozoic (Caxito et al., 2017, 2016).

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#### 418 5.4. A model for IOCG mineralization in the Riacho do Pontal Mineral District

419 Pioneering studies on the Caraíba Cu deposit within the Vale do Curaçá Mining District 420 emphasized orthomagmatic processes as responsible for the genesis of Cu 421 mineralization (Lindenmayer 1981; D'el Rey Silva et al., 1996). Maier and Barnes (1999) 422 noted some unusual aspects the Caraíba deposit shared with other Cu deposits of 423 magmatic origin including: a) the presence of primary sulfides including bornite and chalcopyrite; b) the presence of large amounts (> 50 wt %) of magnetite; c) high Cu/Ni 424 425 ratio ( $\sim$  40); and d) orthopyroxenites with abundant biotite related to shear zones. The 426 importance of metasomatic processes in the genesis of the Caraíba deposit was initially suggested by Rocha (1999) and more recently confirmed by Teixeira et al. (2009), who 427 428 proposed that the type of mineralization in the Vale do Curacá Copper District is 429 analogous to other IOCG deposits documented worldwide. Since then, a number of 430 studies (Teixeira et al. 2010; Hühn et al. 2014; Juliani et al. 2016; Hühn and Silva, 2018; 431 Garcia et al. 2018; Teixeira et al. 2010) confirmed the IOCG nature of the Riacho do 432 Pontal copper occurrences based on: a) their association with potassic and albite 433 alteration, b) the hydrothermal and epigenetic origin of copper ore, which is closely 434 associated with shear zones; c) the presence of hydrothermal iron oxides spatially and 435 temporally related to copper orebodies, d) the fact the copper mineralization is not 436 spatially related to granites, and e) isotopic and whole-rock geochemical analyses 437 related to IOCG deposits.

438 Hydrothermal alteration has led to a pervasive calcic-potassic and calcic-ferric 439 overprint of the host gneisses and migmatites (Hühn et al. 2014). Early-stage sodic 440 hydrothermal alteration is distal in relation to areas with calcic-potassic and potassic-441 ferric alterations, which are present where rocks exhibit higher strain deformation. 442 Hydrothermal alteration processes led to a replacement of metamorphic minerals within foliated gneiss to a suite of minerals including albite, biotite, hematite and 443 amphibole. The replacement minerals are spatially connected to penetrative shear 444 445 deformation and ore plunge along stretching lineation (Hühn and Silva, 2018). Pyrite, 446 hematite, chalcopyrite and chalcocite are related to the ore zones. Magnetite typically 447 occurs in association with the Cu-ore minerals and constitutes less than 1% of the 448 paragenesis (Garcia et al., 2018).

Magnetic and gravity anomaly signatures related to magnetite and hematite-rich Cu ore zones have led researchers to use these data as an effective exploration tool to find new IOCG deposits (Smith, 2002; Clark et al., 2013; Hayward et al., 2013; Hayward et al., 2016). The occurrences of copper at Riacho do Pontal Deposit are positioned at magnetic-field lows. This observation is explained by the fact that the mineralized zone is related to hematite zones in which the content of iron oxide is low (< 2%).

455 World-class IOCG deposits express their metallogenic footprint in different 456 tectonic settings with variable volumes and metal endowments (Hitzman et al., 1992; 457 Pollard et al., 2018; Barton, 2014; Groves et al., 2010). Convergent settings represent propitious tectonic environments for the development of Cu ores (Piraino, 2016). The 458 459 Riacho do Pontal Cu deposits are hosted in a sedimentary formation that have been 460 deposited in a convergent setting (Fig. 8C). This suggests that the Cu forming the IOCG 461 deposits of the Riacho do Pontal Mineral District was sourced by subduction related Cu-462 rich porphyry and was later remobilized by hydrothermal processes.

The general hydrothermal zoning pattern for IOCG deposits is usually vertical,
from magnetite-dominant at depth to hematite-dominant at upper levels. It is possible to
interpret the Neoproterozoic Riacho do Pontal District as positioned in the shallowest
portion of the IOCG system. In this way, additional work should be performed by
searching for deeper (or more eroded) areas of the IOCG system related to more

- 468 magnetic and denser areas, such as those identified to the north of the Riacho Seco area.
- Finally, the potential for discoveries of IOCG deposits related to the collision zone
- between the São Francisco Craton and the Borborema Province has a high potential and
- 471 exploratory work needs to be carried out systematically.

#### 472 6. Conclusions

473 The combined petrographic and <sup>40</sup>Ar-<sup>39</sup>Ar geochronological analyses presented in this 474 study suggest that the age of Cu mineralization in the Riacho do Pontal Mineral District 475 occurred during the Neoproterozoic, around 691 Ma. Zircon grains from the host rock 476 indicate that the protolith has a maximum depositional age of ca. 2035 Ma and was later 477 affected by a late Neoproterozoic to Cambrian metamorphic event potentially related to 478 the building of the Riacho do Pontal Orogen as a result of the collision between the São 479 Francisco Craton and the Borborema Block. The detrital zircon grains also suggest that the deposition of the protolith occurred in a convergent setting which could have 480 481 favored the formation of Cu-rich porphyry that provided a source for the Neoarchean Cu 482 mineralization. Together with literature data, our results depict the Cu ore deposits of 483 the Riacho do Pontal Mineral Province as a typical iron oxide-copper gold (IOCG) 484 deposits. This further suggests that other Brasiliano/Panafrican belts could host this 485 important type of mineralization.

- 485 important type of n
- 486
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- The access to the samples used for this study was granted by the Vale company.
- 490 DATA AVAILABILITY
- 491 Datasets related to this article can be found in the Appendices.
- 492

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#### 815 FIGURES CAPTION

#### 816 **Figure 1. Tectonic subdivisions of the São Francisco Craton.**

- A. Schematic West Gondwana reconstruction of the main tectonic elements of South
- 818 America and Africa. Modified after (Cordani et al., 2016). A: Amazonian Craton; C: Congo
- 819 Craton; SF: São Francisco Craton; WA: West African Craton. BP: Borborema Province. **B**.
- 820 Main structural units of the São Francisco Craton and location of the Minas Basin. ISCA:

821 Itabuna-Salvador-Curaça. Modified after (Alkmim and Marshak, 1998; Barbosa and
822 Barbosa, 2017; Barbosa and Sabaté, 2004).

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#### Figure 2. Main geological features of the study area.

A. Riacho do Pontal copper district. B. Vale do Curaçá copper district. Major copper
 mines, structures and occurrences are shown on the map.

#### 828 Figure 3. Geological map of Riacho do Pontal IOCG District.

Riacho do Pontal SW-NE showing drill holes RIA4-DH001 and RIA4-DH002. Samples
collected along drill holes are highlighted.

#### 832 **Figure 4. Geochemical characterization of biotite grains.**

- A. Biotite types. **B.** Source of biotite. Plots after Nachit et al. (1985) and Foster (1960).
- 834

831

- Figure 5. Spectrum of apparent <sup>40</sup>Ar-<sup>39</sup>Ar ages for sample PCB-SBH-02 (biotite
   hydrothermal ore zone).
- 837

# 838 **Figure 6. Cathodoluminescence images of representative zircon grains.**

- 839 Red circles indicate the location of analyses. Ages correspond to concordia dates (A, B) 840 and  ${}^{207}\text{Pb}/{}^{206}\text{Pb}$  dates (C), with uncertainties given at the  $2\sigma$  level. **A**. Sample DH001-841 003. **B**. Sample DH002-009. **C**. Sample DH001-0010.
- 842

# 843 **Figure 7. Geochronological diagrams.**

- Wetherill diagrams were generated using IsoplotR (Vermeesch, 2018). Error ellipses are 844 depicted at the  $2\sigma$  level. Analyses used to calculate the Maximum Depositional Age 845 846 (MDA) are depicted in dark blue. Other concordant analyses are depicted by pale blue. 847 The weighted mean error ellipse (concordia date) of the youngest cluster of concordant 848 grains is depicted in pink. Analyses used to regress the data for intercept date 849 calculations are depicted in green. N<sub>a</sub>: number of analyses performed for each sample; 850 N<sub>zrc</sub>: number of analyzed grains. MSWD: Mean Square Weighted Deviate (given for both concordance and equivalence when referring to a concordia date); Prob.: probability for 851 852 concordance and equivalence. A. Wetherill diagram for sample DH001-003. B. Age distribution for sample DH001-003, generated with Density plotter (Vermeesch, 2012). 853 Bin width: 10 Ma, bandwidth: 8 Ma. Open circles indicate individual analyses. C. 854
- Wetherill diagram for sample DH002-009. **D.** Wetherill diagram for sample DH001-0010.
- 857

#### 858 **Figure 8. Age probability distribution and tectonic discrimination diagrams.**

- The histograms were generated with a bin width of 10 Ma. The kernel densities were
- 860 estimated using a bandwidth of 12 from concordant ages. The open circles below each
- diagram denote the individual analyses used to generate the diagrams (using Density

- 862 Plotter; Vermeesch, 2012). N: number of analyses. **A.** Dataset from this study. **B.**
- 863 Formosa Formation (Caxito et al., 2014a). **C.** Tectonic discrimination diagram (Barham
- 864 et al., 2022).
- 865

#### 866 APPENDICES

- 867 Appendix A. Drill-core location and sampling depth.
- 868 Appendix B. 40Ar-39Ar analytical results.
- 869 Appendix C. U-Pb zircon analytical results.