Sulfide recrystallization and gold remobilization during the 2.0 Ga stage of the Minas Orogeny: implications for gold mineralization in the Quadrilátero Ferrífero area, Brazil

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Abstract

The historical Quadrilátero Ferrífero (QF) mining district in Brazil is a poly-deformed Archean terrane recording several tectonic events. This history has hampered the accurate dating of its important gold deposits given that most of the geochronological clocks have been affected by multiple thermal events. In an attempt to determine an accurate time constraint for the mineralizing events in this region, we provide the first Re-Os dating for a gold deposit in the QF, obtained from 13 mineral separates of disseminated sulfide phases (pyrrhotite, coarse-grained arsenopyrite, fine-grained arsenopyrite, pyrite) at the recently discovered São Sebastião deposit (NW QF). Three distinct successive sulfidation stages are interpreted at the deposit. The final stage, texturally associated with gold, is marked by fine-grained arsenopyrite and pyrite (assemblage III) and is associated with high-temperature (~600°C) features. A Re-Os errorchron is obtained when considering the data of all samples collectively, but a comprehensive Re-Os isochron age of 1987 ± 72 Ma (2σ; n = 4; IsoplotR model 3; initial $^{187}Os/^{188}Os$ = 2.1 ± 0.7) is obtained from assemblage III. A ^{187}Re-$^{187}Os^r$ isochron at 1988 ± 56 Ma (MSWD = 0.1, initial $^{187}Os^r$ = -0.1 ± 2.6 ppt; n=4) is obtained if an initial $^{187}Os/^{188}Os$ composition of ca. 2.1, is used, this being consistent with the fact that the ^{187}Os in the sulfides in assemblage III is largely radiogenic ($^{187}Os^r$). Earlier assemblages (I and II) individually show variable initial $^{187}Os/^{188}Os$, indicative of disturbance to the Re-Os systematics at ~2.0 Ga. This age is considered to be the best estimative for the timing of gold mineralization at São Sebastião, being coincident with the waning stages of the Minas Orogeny, the thermal effects of which are restricted to the southern QF. Hence, we consider that the hot fluids from which assemblage III crystallized were responsible for resetting the Re-Os systematics in assemblages I and II, and were central to Paleoproterozoic gold deposition in the region. This ~2.0 Ga age challenges previous notions of a late Archean,~2.7 Ga, mineralizing event in the QF and makes it possible that gold remobilization occurred elsewhere in the region, particularly in areas representing deeper crustal levels.

Introduction

The Quadrilátero Ferrífero (QF, **Fig. 1**) area in the southern São Francisco Craton, Brazil, has experienced extensive gold production since the 18th century. The superposition of tectonic events in the QF hampers the acquisition and interpretation of absolute isotopic ages of gold mineralization (Lobato et al., 2001b; Lobato et al., 2007). This is further complicated by the presence of different mineralization styles, ages and host-rocks (Renger et al., 1993; Cabral, 1996; Cabral et al., 2001; Lobato et al., 2001 a,b; Koglin et al., 2012; Cabral et al.,2013; Cabral

et al., 2015; Tassinari et al., 2015; Brando Soares et al., 2018; Fabricio-Silva, 2019). As a result, the timing of gold ore formation in the QF is debated. Most of the gold occurrences in this region, including the word-class Cuiabá and Morro Velho deposits (see location in **Fig. 1**), are classified as orogenic gold systems and are hosted within the 2.90-2.73 Ga Rio das Velhas greenstone belt (RVGB - Machado and Carneiro, 1992; Schrank et al., 2002; Hartmann et al., 2006; Noce et al., 2007; Baltazar and Zucchetti, 2007; Vial et al., 2007; Martins et al., 2016; Moreira et al., 2016). The aforementioned gold systems are described as being late- to post-tectonic, slightly postdating the 2.70 - 2.65 Ga peak metamorphism related to the waning stages of the Rio das Velhas orogenic event (2.8 - 2.75 Ga; Lobato et al. 2001b; 2007; Baltazar and Zucchetti, 2007; Noce et al., 2007).

Various imprecise Pb-Pb model ages for galena, arsenopyrite and pyrite are reported between 2.7 and 1.9 Ga (Thorpe et al., 1984) for the São Bento and Morro Velho deposits in the RVGB (see **Fig. 1** for location). These ages are interpreted to reflect the onset of gold deposition (2.67 - 2.65 Ga), as well as later recrystallization events (2.1-1.9 Ga) (Lobato et al., 2001a). The younger ages are commonly related to the Minas Orogeny, a 2.47-2.10 Ga Paleoproterozoic compressive event responsible for arc-amalgamation to the south of the QF during the Rhyacian-Orosirian (Alkmim and Teixeira, 2017) and correlative with the 2.2 – 2.0 Ga Eburnean Orogeny in western Africa (McFarlane et al., 2019 and references therein). Similar ages between 2.1 and 1.9 Ga are reported for the Turmalina deposit, located west of the RVGB in the correlative Pitangui greenstone belt (PGB; **Fig.1**). At Turmalina, these ages are calculated from Sm-Nd, Rb-Sr and secondary Pb-Pb isotopic studies in garnet, sericite, pyrrhotite and from arsenopyrite associated with gold mineralization (Tassinari et al., 2015).

The first reliable and precise geochronological data for the timing of gold mineralization in the QF was obtained by U-Pb SHRIMP dating of accessory monazite in association with gold at the Morro Velho and Cuiabá deposits (Lobato et al., 2007). Data from both deposits yielded a 2672 ± 14 Ma U-Pb age (Lobato et al., 2007). A further U-Pb SHRIMP ca. 2.7 Ga age (2730 ± 42 Ma; upper intercept) is reported from hydrothermal monazite within the sulfide-rich zone of the Lamego deposit, nearby Cuiabá (Martins et al., 2016). Younger U-Pb SHRIMP ages of 2387 ± 46 Ga (monazite; upper intercept) and 518.5 ± 9 Ma (xenotime; Concordia age) that are coincident with the timing of the Minas (2.47-2.1 Ga) and Brasiliano (0.65-0.50 Ga) orogenies, respectively, are also reported from the Lamego deposit.

The rhenium-osmium (Re-Os) isotope system has long been used to date molybdenite, containing significant concentrations of Re (ppm) and no common Os (Morgan et al., 1968; Markey et al., 1998; Markey et al., 2007). Improved chemical separation and analytical methods (Creaser et al., 1991; Shirey and Walker, 1995) have permitted the measurement of Os and Re at lower concentrations (ppb level Re and ppt level Os) enabling other sulfides (e.g., pyrite, arsenopyrite, chalcopyrite, bornite, carrolite, cobaltite, löllingite) to be utilized as reliable Re-Os geochronometers (e.g., Stein et al., 1998b; Stein et al., 2000; Arne et al., 2001; Barra et al., 2003; Morelli et al., 2005; Feng et al., 2009; Huang et al., 2015; Hnatyshin et al., 2015; Ding et al., 2016; Saintilan et al., 2017a,b; 2018). Importantly, the Re-Os system allows dating of sulfide minerals that are directly associated with the ore (e.g., gold), without the need to make inferences through the dating of other gangue minerals, which may have had a more complex history (Stein et al., 1998a; Mathur et al., 1999; Morgan et al., 2000; Stein et al., 2000; Arne et al., 2001).

Here, we present here the first direct Re-Os dating for sulfides in the QF to provide an improved temporal and genetic understanding of gold mineralization in the district. Specifically, we present Re-Os analyses of pyrrhotite, arsenopyrite, and pyrite from the recently discovered (2014) São Sebastião gold deposit in the PGB. The Re-Os data permit a discussion regarding the complex timing and genesis of the gold deposits in this region and helps to provide insights into the timing and conditions of gold deposition in other areas that record the superposition of various tectonic events. This is especially relevant in late Archean and Paleoproterozoic terrains, known globally as the preferred hosts to orogenic-gold deposits.

Regional Geology

The ca. 3.2 – 2.6 Ga Archean terrane of the QF is composed of TTG-granite complexes and greenstone belts and records a complex geological history (Lana et al., 2013; Teixeira et al., 2017; Simon et al., 2018) (**Fig. 1** - Dorr, 1969; Alkmim and Marshak, 1998). This includes; (I) the Neoarchean Rio das Velhas orogenic event (2.80 - 2.75 Ga – Baltazar and Zucchetti, 2007 and references therein), a progressive regional deformational event dominated by thrust tectonics ($D_n + D_{n+1}$); (II) the accretionary Paleoproterozoic Minas Orogeny (2.47 - 2.10 Ga; Alkmim and Teixeira, 2017 and references therein), also known as the Transamazonian event, which has occurred to the south of the QF and caused the exhumation of TTG-granite domes during the orogenic collapse, interpreted from a dome-and-keel architecture (Alkmim and Teixeira, 2017; Cutts et al., 2019); and (III) the Neoproterozoic Brasiliano-Pan African Orogeny (0.65 – 0.50 Ga;

e.g., Brito Neves et al., 2014) affecting the E border of the QF close to the Araçuaí (Chemale et al., 1994; Alkmim and Marshak, 1998) marginal orogenic belt.

To date, the gold deposits in the RVGB (the main greenstone belt in the QF) have been traditionally classified as epi- (150 – 300 ^{o}C, < 6 km) to mesozonal (300 – 475 ^{o}C, 6 - 12 km) orogenic-gold systems (Lobato et al., 2001 a,b). The fluids responsible for such mineralization are described as having originated from metamorphic dehydration at 300 – 350 ^{o}C, typical of many other greenschist-metamorphosed Neoarchean terranes (Gebre-Mariam et al., 1995; Groves et al., 1998; McCuaig and Kerrich, 1998; Jia et al., 2003; Goldfarb and Groves, 2015). In contrast, the gold deposits in the correlative PGB (**Fig.1**) display high-temperature (500 - 600°C) features (Brando Soares et al., 2018; Fabricio-Silva et al., 2019) being hosted by rocks metamorphosed at amphibolite-facies conditions. Such characteristics are typically related with those of deeper hypozonal (475 – 700 ^{o}C, >12 km) gold deposits.

Sulfide mineral paragenesis at São Sebastião

São Sebastião is a stratabound, hypozonal gold deposit hosted by 2859 ± 11 Ma banded iron formation (BIF) layers. The deposit is composed of two main orebodies (Biquinho and Pimentão) and a satellite body (Tomate) exhibiting a saddle reef-like structure (see **Fig. 2A**). Gold is contained within sulfide-rich intervals that are spatially associated with D_n and D_{n+1} folds and thrust-related shear zones formed during the NE-SW shortening related to the 2.80 - 2.75 Ga Rio das Velhas orogeny.

A recent detailed petrographic study of the sulfide paragenesis identifies at least three disseminated sulfidation stages at São Sebastião and a late stage of vein formation (Brando Soares et al., 2018; see **Fig. 2** for main textures and paragenesis). Sulfide assemblage I comprises disseminated pyrrhotite and chalcopyrite directly associated with structural features related to an early compressional event (**Fig. 2B, 2C, 2D, 2E**). Sulfide assemblage II is related to coarse-grained arsenopyrite and rare arsenian pyrite. Coarse-grained arsenopyrite pervasively replaces assemblage I pyrrhotite (**Fig. 2C, 2D**). Sulfide assemblage III comprises localized fine-grained arsenopyrite, (As-free) pyrite, quenched Cu-Fe-S intermediate solid solution phase (ISS), plus minor pyrrhotite and chalcopyrite (**Fig. 2B, 2C, 2F, 2G, 2H, 2I**). The quenched ISS occurs in the form of irregular pyrrhotite-chalcopyrite intergrown patches only recognized by SEM-EDS (**Fig. 2F**). The fine-grained arsenopyrite possibly results from the recrystallization of assemblage II coarse-grained arsenopyrite (**Fig. 2C, 2G, 2H**). Sulfide assemblage III is restricted to the inner sections of the ore bodies (see **Fig. 2A**). Gold is found as inclusions in pyrite, filling fractures in

143 pyrite and both coarse- and fine-grained arsenopyrite and in the form of late droplets and
144 coarser grains at the contact between sulfides and gangue minerals predating vein formation
145 (**Fig. 2G, 2H, 2I**). The post-ore quartz-sulfide veins contain the youngest generation of pyrite
146 and chalcopyrite (**Fig. 2E**). Small-scale localized brittle-shearing features are recognized in
147 association with assemblage III and post-ore veinlets (see **Fig. 2D** at the bottom right corner). A
148 paragenetic table is available in **Fig. 2J**.

149 Assemblage III is considered to have crystallized from high-temperature (~600°C) Bi-
150 enriched melts. These were responsible for the destabilization of previous assemblages as well
151 as the scavenging and re-concentration of gold, and are considered to have had the major
152 impact on ore formation (see native gold in **Figs. 2G, 2I** and Brando Soares et al., 2018). The
153 overprint of sulfide paragenesis and its role in ore formation at São Sebastião is also evidenced
154 by geochemical trends from whole-rock assays. General low to medium gold grades (10 to 6000
155 ppb) are identified in samples displaying only sulfide assemblage I, where enhanced grades are
156 associated with increases in S, Ag, Cu and Bi. A second trend is recognized in samples displaying
157 the sulfide assemblage III overprint exhibiting variable Au grades (60 to 45000 ppb) and
158 constant high S, Ag, Cu and Bi concentrations. Notably, the highest gold grades (5000 to 45000
159 ppb) occur in samples where the two geochemical trends and sulfide assemblages overlap,
160 suggesting a process of gold remobilization and re-concentration triggered by the formation of
161 sulfide assemblage III.

162 **Sampling and methodology**

163 Thirteen sulfide mineral separates were obtained from various drill-core samples from
164 within the main mineralized section at the São Sebastião deposit (Biquinho body, **Fig.2A**). The
165 thirteen mineral separates comprise disseminated assemblage I pyrrhotite (n = 4), assemblage
166 II arsenopyrite (n = 4), and assemblage III arsenopyrite and pyrite (n = 5). Samples # 5 and 10
167 are composed of mix of very fine-grained (200-500 μm) assemblage III arsenopyrite and pyrite
168 that could not be separated by the conventional methods described below.

169 The drill core samples (15-20 cm- long) were first crushed in an agate ball mill to prevent
170 any metal contamination, followed by Frantz magnetic separator, heavy liquids (2.89 g/cm^3
171 bromoform) and, finally purified by handpicking using a binocular microscope. For samples #4
172 #6 and #13, before handpicking, a large amount of fine arsenopyrite not extracted by Frantz
173 was separated from pyrite of similar grain size by decantation velocity when immersed and
174 agitated in heavier diiodomethane (3.32 g/cm^3). This technique was developed for this work

175 and is referred to as the "Wyatt technique". This method is based on the density contrast

176 between arsenopyrite (6.07 g/cm^3) and pyrite (5.01 g/cm^3). A sample (weighting approximately

177 1 gram) containing both minerals in a very fine granulometry (200-500 μm), being very difficult

178 to handpick, was separated in 4 regular 15 mL test tubes. Each tube was filled with

179 diiodomethane up to 2 cm from the top. Each mixture in the test tubes was agitated with a glass

180 rod immediately before the bottom of the tube was rapidly frozen using liquid nitrogen. As a

181 result, the denser fraction (i.e., arsenopyrite) was concentrated within the frozen bottom after

182 a few seconds (e.g., 10 s). The light fraction composed mainly of pyrite was washed out of the

183 tubes using acetone and collected in a filter paper. The denser phase was collected the same

184 way after the diiodomethane had thawed. The purity of the separates was improved by

185 handpicking under a light microscope.

186   The sulfide samples were then analyzed at the Source Rock and Sulfide Geochronology

187 and Geochemistry, and Arthur Holmes Laboratories in the Durham Geochemistry Center at

188 Durham University, UK, following the procedure described in Selby et al. (2009). Each sample

189 (~0.4 g) was loaded in a Carius tube with a known amount of mixed ^{185}Re and ^{190}Os tracer

190 solutions and then dissolved and homogenized with a mix of concentrated hydrochloric (3 mL)

191 and nitric (6 mL) acid at 220 °C for 48 h. The Os was extracted from the acid solution using

192 solvent extraction (CHCl$_3$) and purified by microdistillation (Birck et al., 1997). The Re fraction

193 was isolated using a NaOH-acetone solvent extraction and further purified by standard HCl-

194 HNO$_3$ anion-bead exchange chromatography (Selby and Creaser, 2003). The purified Re and Os

195 fractions were loaded on Ni and Pt filaments, respectively, and analyzed using a Thermo

196 Scientific Triton thermal ionization mass spectrometer in negative mode (N-TIMS). Total

197 procedural blanks for Re and Os were 2.3 ± 0.2 pg (picogram) and 1.00 ± 0.02 pg, respectively,

198 with an average ^{187}Os/^{188}Os value of 0.17 ± 0.06 (n = 2). Two level absolute uncertainties are

199 calculated using error propagation and include Re and Os mass spectrometer measurements,

200 blank abundances and isotopic compositions, spike calibrations, weighing uncertainties of

201 sample and tracer solution, and reproducibility of standard Re and Os isotope values. The Re-

202 Os isotopic data including the 2σ propagated uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os and

203 the associated error correlation function (rho) were used to calculate a Re-Os isochron age

204 using York regression via Isoplot v. 4.15 and IsoplotR with a λ ^{187}Re constant of 1.666 x10^{-11} yr$^-$

205 ^{1} (Smoliar et al., 1996; Ludwig, 2012, Vermeesch, 2018).

Re-Os geochronology results

207   All Re-Os data for the thirteen samples analyzed are presented in **Table 1** and is also

208 available as an appendix file (**Appendix Table A1**). Assemblage I pyrrhotite possesses between

209 ca. 0.24 and 0.98 ppb Re and ca. 18 and 74 ppt Os, and $^{187}Re/^{188}Os$ of ca. 56 to 96 and $^{187}Os/^{188}Os$

210 of 2.1 to 3.9. In contrast, assemblage II arsenopyrite (Re = 7-14 ppb, Os = 192-416 ppt,

211 $^{187}Re/^{188}Os$ = 442-1454, $^{187}Os/^{188}Os$ = 16.3-53.2) and assemblage III arsenopyrite/pyrite (Re = 2-

212 11 ppb, Os = 75-369 ppt, $^{187}Re/^{188}Os$ = 489-608, $^{187}Os/^{188}Os$ = 18.6-22.6) show considerably

213 more elevated Re-Os concentrations and isotopic compositions.

214   The absolute timing of mineralization and the temporal duration between assemblages

215 I, II, III at the São Sebastião deposit is unknown. The relative age of the mineralization from

216 oldest to youngest based on petrographic observations is assemblage I to III. Firstly, we evaluate

217 the Re-Os isotope systematics of the entire thirteen samples based on the premise that the

218 sulfide assemblages are broadly contemporaneous. Collectively the Re-Os isotope data for

219 assemblage I pyrrhotite, and assemblage II and III arsenopyrite and pyrite scatter about a ca.

220 2.2 Ga errorchron (2151 ± 86 Ma; 2σ; MSWD = 375; n = 13; York model 3; initial $^{187}Os/^{188}Os$ =

221 0.08 ± 0.89; **Fig. 3A**). Given that the sample set represents a number of samples (n = 4 to 5) from

222 each assemblage (**Table 1; Appendix Table A1**), we consider that this excess data-point scatter

223 is unlikely to represent an analytical artifact. Instead, the scatter about the best-fit of all the Re-

224 Os isotope data likely reflect disparate temporally distinct sulfide generations, with, or without,

225 variable initial $^{187}Os/^{188}Os$ ratios (Osi), and/or disturbance to the Re-Os systematics. These

226 issues invalidate the isochron dating approach for the entire sample set collectively.

227   Errorchrons are also produced individually for the Re-Os isotope data for assemblage I

228 (1989 ± 3900 Ma; 2σ; MSWD = 298; n = 4; York model 3; initial $^{187}Os/^{188}Os$ = 0.1 ± 5.8; **Fig. 3B**)

229 and II (2187 ± 340 Ma; 2σ; MSWD = 224; n = 4; York model 3; initial $^{187}Os/^{188}Os$ = -1.1 ± 5.3; **Fig.

230 3C**). In contrast, the Re-Os isotope data for assemblage III yield a significantly better linear fit

231 (MSWD = 31), but still an imprecise age (2005 ± 980 Ma; 2σ; n = 5; York model 3; initial

232 $^{187}Os/^{188}Os$ = 2.2 ± 9.0; **Fig. 3D**). For assemblage III, the scatter about the linear best-fit of the

233 Re-Os data is predominantly controlled by sample #13 that plots above the line of best-fit.

234 Excluding sample #13, the remaining assemblage III (n = 4) Re-Os data yields a Re-Os isochron

235 age of 1989 ± 347 Ma (2σ; MSWD = 2.3; n = 4; York model 3; initial $^{187}Os/^{188}Os$ = 2.1 ± 3.2; **Fig.

236 3d**). To account for the scatter in the Re-Os data, the model 3 approach of Isoplot introduces a

237 normal distributed variation in the initial $^{187}Os/^{188}Os$ (Ludwig, 2011). In a similar approach to

238 account for the scatter in the best-fit of the Re-Os data, IsoplotR (Vermeesch, 2018) utilizes a

non-normal variation in the initial $^{187}Os/^{188}Os$, which results in a more precise Re-Os isochron age (1987 ± 72 Ma; 2σ), with a smaller uncertainty in the initial $^{187}Os/^{188}Os$ (2.1 ± 0.7; variation in initial $^{187}Os/^{188}Os$ = 0.00075 + 0.139310 / - 0.000075 [2s]).

Considering an initial $^{187}Os/^{188}Os$ composition of ca. 2.1 for assemblage III, as given by the Re-Os isochron, >89 % of the ^{187}Os in the assemblage III sulfides is radiogenic ($^{187}Os^r$) (**Table 1; Appendix Table A1**). A ^{187}Re-$^{187}Os^r$ isochron age for assemblage III, based on $^{187}Os^r$ calculated using an initial $^{187}Os/^{188}Os$ composition of ca. 2.1 is 1998 ± 55 Ma (2s; Model 1, MSWD = 1.4; n = 5; initial $^{187}Os^r$ = 0 ± 2.6 ppt), or 1988 ± 56 Ma without sample #13 (Model 1, MSWD = 0.1, initial $^{187}Os^r$ = -0.1 ± 2.6 ppt; **Fig. 3e**). Collectively, the Re-Os data for assemblage III provide the best estimate for the timing of mineralization for this sulfide stage at ca. 2.0 Ga. For the Re-Os data of sample #13 to return a ca. 2.0 Ga age, the $^{187}Os^r$ must be calculated using an initial $^{187}Os/^{188}Os$ of ca. 3, which would explain why sample #13 falls off the best-fit of all other assemblage III points on the $^{187}Re/^{188}Os$ vs. $^{187}Os/^{188}Os$ plot (**Fig. 3**).

If it is considered that assemblage II initially formed broadly contemporaneously and prior to the 2.0 Ga assemblage III, the scatter about the best-fit of all the assemblage II $^{187}Re/^{188}Os$ vs. $^{187}Os/^{188}Os$ data likely reflects disturbance to the Re-Os arsenopyrite systematics at ca. 2.0 Ga. This is illustrated by the range of model ages for assemblage II calculated from the same initial $^{187}Os/^{188}Os$ composition (**Table 1; Appendix Table A1**). Akin to assemblage III, the ^{187}Os budget of assemblage II is dominated by $^{187}Os^r$ (>90 %; **Table 1; Appendix Table A1**). Model ages for assemblage II overlap (including uncertainty) with the timing of assemblage III (ca. 2.0 Ga) based on $^{187}Os^r$ calculated from initial $^{187}Os/^{188}Os$ compositions of 0.12 and 0.5 (samples #1, 2), 1.0 (samples #1, 2, 3), 1.5 (samples #3, 11) and 2.0 (sample #11) (**Table 1; Appendix Table A1**). The latter suggests that the disturbance to the Re-Os isotope systematics resulted in the arsenopyrite of assemblage II possessing variable initial $^{187}Os/^{188}Os$ ratios (Osi). A similar conclusion of Re-Os isotope disturbance can be made for the assemblage I pyrrhotite. Only samples #7 (Osi = 0.5) and #9 (Osi = 0.12) (**Table 1; Appendix Table A1**) return Re-Os model ages in line with those given by assemblage III (ca. 2.0 Ga). The remaining samples (#8 and 12) all yield ages younger than the 2.0 Ga assemblage III, suggesting that the Re-Os systematics did not close at 2.0 Ga, but have been affected by a younger geological event.

Discussion and implications for the timing of gold mineralization at São Sebastião

Timing relates to Au mineralization and Au upgrading

The Re-Os data for sulfide assemblage III provide the best estimate for the timing of mineralization at São Sebastião at ca. 2.0 Ga. This age corresponds with the waning stages of the Minas Orogeny, an accretionary event characterized to the south of the QF in the allochthonous Mineiro belt (2.47 - 2.10 Ga – Ávila et al., 2010; Teixeira et al., 2015; Alkmim and Teixeira, 2017). This Paleoproterozoic age is quite distinct from the 2672 ± 14 Ma U-Pb age obtained for accessory monazites in the Cuiabá and Morro Velho deposits of the RVGB (Lobato et al., 2007).

Certain tectonic features recognized in the QF, such as the Pará de Minas shear zone in the PGB (**Fig. 1** – Tassinari et al., 2015), are also associated with this time interval (2.1 to 1.9 Ga) and possibly relate to the gravitational collapse of the Minas orogen (Alkmim and Teixeira, 2017) further to the south. Such structures are interpreted to have reactivated older Archean crustal discontinuities resulting in a Paleoproterozoic dome-and-keel architecture (Alkmim and Marshak, 1998; Cutts et al., 2019). This process is driven by means of crustal thinning and uplift of hot (600 – 700 ^{o}C) mid-crustal (20 km) Archean gneiss domes (Alkmim and Marshak, 1998; Cutts et al., 2019). The thermal effect of this extensional collapse event is reported by regional resetting of 2100 - 1940 Ma U-Pb ages in titanite and monazite, implying temperatures in the order of ca. 600 – 700 ^{o}C (Aguilar et al., 2017) at this time. This temperature range is considered as the minimum closure temperature for such accessory minerals (Scott and St-Onge, 1995), but is lower than the temperature necessary to disturb/reset the U-Pb systematics of zircon (≥ 700 ^{o}C – Lee et al., 1997; Rubatto et al., 2001; Hermann and Rubatto, 2003). The absence of ca. 2.1 Ga U-Pb zircon reset ages in the QF (Romano et al., 2013; Farina et al., 2015; Albert et al., 2016; Aguilar et al., 2017) supports this temperature constraint.

The U-Pb age range in titanite and monazite is very similar to that obtained from the Re-Os analyses of sulfide assemblage III in this study. Moreover, temperatures around ca. 600 ^{o}C, as implied from the U-Pb systematics and ages of monazite and titanite in the QF (e.g., Aguilar et al., 2017), are high enough to cause sulfide recrystallization (e.g. Cook et al., 2009) driven by hydrothermal dissolution and re-precipitation, such as is observed in the São Sebastião gold deposit. In this regard, the sulfide assemblage III is described to have formed at a similar temperature (ca. 600 ^{o}C) based on the arsenopyrite geothermometer, ISS formation and crystallization of exotic Bi-sulfosalts of the pavonite group (see Brando Soares et al., 2018). This further indicates a possible correlation between the formation of assemblage III and the waning stages of the Minas Orogeny at ca. 2.0 Ga, in a broader regional perspective. As a result, the Re-

302 Os systematics of the early sulfide assemblages (I and II) at São Sebastião may have been reset

303 by higher-temperature fluid fluxes at 2.0 Ga. This being also coeval (within uncertainty) with

304 the sulfide recrystallization evident in assemblage III. For instance, the Re-Os system in

305 arsenopyrite has been shown to be preserved up to temperatures as high as 400 $^{\circ}$C, and

306 possibly exceeding 450 $^{\circ}$C (Morelli et al., 2010), but is expected to be reset at higher

307 temperatures.

308   The highest gold grades at São Sebastião, which are associated with assemblage III, were

309 developed preferentially in sites where gold was re-concentrated/upgraded from sulfide

310 assemblages (I) and (II). This is shown both by petrography and by two distinct whole-rock

311 geochemical trends (see **Section 2**). Thus, gold remobilization at São Sebastião is associated

312 with the high-T recrystallization of sulfides at ca. 2.0 Ga, yielding assemblage III comprising

313 mainly fine-grained arsenopyrite and pyrite. This sulfide recrystallization stage is accompanied

314 by infills of native gold and native bismuth in fractures of arsenopyrite (both coarse- and fine-

315 grained) and pyrite, where Au and Bi remained in the liquid phase until the low cooling

316 temperature of 271°C (Brando Soares et al., 2018). Since gold fills fractures in recrystallized

317 sulfides, we propose that the final crystallization of native gold slightly postdates these phases.

318   Overall, the timing for gold mineralization proposed in this study (ca. 2.0 Ga) is

319 consistent, in part, with the proposals of Tassinari et al. (2015). They advocated a ca. 2.0 Ga

320 sulfidation and gold-mineralizing stage at the Turmalina deposit, near to São Sebastião.

321 However, remobilization from a previous Archean assemblage was not considered. Here, gold

322 remobilization from a Neoarchean sulfide-rich paragenesis triggered by sulfide recrystallization

323 is proposed, similar to that described in the Western Churchill Province, Canada (Lawley et al.,

324 2015). This is supported by petrographic observations and whole-rock geochemistry indicating

325 Au-enrichment in zones of overprinted sulfide assemblages, as well as contrasting initial

326 ^{187}Os/^{188}Os (Os$_i$) ratios between the early and late sulfide subsets marking the reset of the Re-

327 Os isotopic clock in the earlier paragenetic sequences. Given that the sulfide recrystallization

328 likely occurred during Paleoproterozoic times, gold remobilization is assumed to be of the same

329 age. Moreover, at São Sebastião, we emphasize that the hypozonal features of the

330 mineralization were attained during at ca. 2.0 Ga at ca. 600 $^{\circ}$C, which is equivalent with depths

331 of > 12 km and amphibolite-facies metamorphic conditions. This is typical of deeply-emplaced

332 gold deposits where the overprints of a late, high-temperature assemblage are usually

333 associated with gold deposition that is either syn- or post-metamorphic (see Bouchot et al.,

334 2005; Tomkins et al., 2006; Tomkins et al., 2007, Hagemann et al., 2013 and Kolb et al., 2015).

335 The São Sebastião sulfide assemblage III is here estimated to have formed at

336 amphibolite-facies conditions during the waning stages of the Minas Orogeny. This, however,

337 requires that the effects of this tectono-thermal event are more widespread than considered

338 in previous literature (Alkmim and Teixeira, 2017). The findings in the present work can be

339 combined with the ca. 2.0 Ga titanite resetting ages reported in the PGB area (Aguilar et al.,

340 2017) to propose an extension of the thermal imprint area of the Minas Orogeny. The actual

341 imprint front is likely to be located approximately 100 km NW from where the 2.1 Ga

342 convergent structures and rocks are recognized (limit between the autochthonous and

343 allochthonous Mineiro Belt in **Fig. 1**).

344 As such, we speculate that the wider thermal effect of the Minas Orogeny is related to

345 deep extensional features caused by the collapse of the Paleoproterozoic orogen (e.g., Aguilar

346 et al. (2017), Alkmim and Teixeira (2017) and Cutts et al. (2019). The high-temperature

347 assemblages imply that the gold deposits in the PGB (São Sebastião, Turmalina) formed at a

348 deeper crustal level compared to the deposits in the RVGB (e.g., world-class Cuiabá), which

349 show epi- to mesozonal characteristics). It is possible, however, that high-T sulfide

350 remobilization also played a role deeper in the RVGB based on ca. 2.1 Ga resetting ages reported

351 for this area at Lamego (Martins et al., 2016). In this sense, further investigation by Re-Os

352 geochronology may provide important insights on the evolution of gold deposits in the south

353 São Francisco Craton, where the reactivation of Archean NW-SE structures may have had an

354 important role in transporting fluids from younger hydrated sources. Remarkably, ca. 2.0 Ga

355 ages are often reported for gold deposits in the West Africa Craton (e.g., Mignot et al., 2017),

356 but have seldom been described in the correlative São Francisco Craton. Dating mineralization

357 events may, therefore, be an important tool to more comprehensively understand the

358 reworking of Archean gold deposits in Brazil and to improve exploration models for similar

359 multistage ore deposits occurring elsewhere in poly-deformed terranes.

Conclusions

361 At the hypozonal São Sebastião gold deposit (Pitangui greenstone belt) in the QF mining

362 district in Brazil, gold is associated with sulfide-rich layers within Archean BIF. Rhenium-osmium

363 geochronometry of the paragenetically youngest sulfide assemblage III provides the best

364 estimate for the timing (ca. 2.0 Ga) of sulfide and gold mineralization at São Sebastião. This age

365 coincides with the waning stages of the Minas Orogeny. The ca. 2.0 Ga age is different to the

366 ages reported for other gold deposits in the nearby Rio das Velhas greenstone belt (ca. 2.7 Ga),

367 but is identical to U-Pb ages obtained previously for titanite and monazite in the QF that are

368 attributed to record the timing of resetting of the mineral U-Pb systematics. This resetting is

369 related to the thermal effects (ca. 600°C) of extensional features resulted to the collapse of a

370 Paleoproterozoic accretionary orogen (Mineiro Belt) known approximately 100 km to the south

371 of São Sebastião. Thus, the late sulfidation stage (assemblage III) at São Sebastião is considered

372 to have formed by recrystallization of the earlier sulfide assemblages, which had their Re-Os

373 systematic reset at ca. 2.0 Ga. Gold is mostly observed filling fractures in arsenopyrite and pyrite

374 and in the form of late droplets and crystals displaying an association with Bi. In addition, the

375 highest gold grades are seen in zones where the early and late sulfide paragenesis overlap. This

376 implies that gold was probably remobilized from the early paragenetic sequence and re-

377 concentrated by the high-T sulfide association in Paleoproterozoic times. The regional

378 implications are that the overprinting thermo-tectonic effects of the Paleoproterozoic (2.47 -

379 2.10 Ga) Minas Orogeny can be traced much further north than previously known. This suggests

380 that important gold occurrences in the neighboring Rio das Velhas greenstone belt, such as the

381 world-class Cuiabá deposit, may also have been regenerated at this time. This is supported by

382 the ca. 2.1 Ga U-Pb age for monazite from the meso- to epizonal sections of these deposits. In

383 turn, this implies that yet undiscovered hypozonal deposits may exist in the RVGB, beneath the

384 currently explored depths. In more general terms it is possible that Paleoproterozoic rocks may

385 represent important targets for gold mineralization in the QF, and indeed the broader São

386 Francisco craton and its correlatives worldwide.

Acknowledgements

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650 **Figure Captions**

651

652 **Figure 1:** Regional geological setting of the Quadrilátero Ferrífero in the south sector of the São
653 Francisco Craton. Map shows the location of São Sebastião (study area marked by dashed
654 rectangle) and other hypozonal gold deposits in the Pitangui greenstone belt, as well as the
655 main gold deposits of various types within the Rio das Velhas greenstone belt.
656 Latitude/longitude geographic coordinates at the corners of the map and UTM in other
657 intersections. Modified from Dorr (1969), Corrêa Neto et al. (2012), Pinto and Silva (2014), and
658 Aguilar et al. (2017).

659

660 **Figure 2:** (A) Transect from a 3D model of the São Sebastião deposit showing the positioning of
661 drill cores and respective lithological correlation. Modified from the São Sebastião 43101 report
662 provided by IAMGOLD Brazil (Mitrofanov and Cole, 2020). (B) to (E) Drill core images from
663 sulfide-rich banded iron formation (BIF) illustrating the various sulfidation stages at São
664 Sebastião (check Fig. 2J for relative timing). (B) assemblage I pyrrhotite and chalcopyrite (po_1 +
665 ccp_1) parallel to the Sn foliation overgrown by arsenopyrite (apy – assemblage II) preferably
666 within organic-matter-rich (darker) microbands. Assemblage III pyrrhotite, chalcopyrite (po_2 +
667 ccp_2) and pyrite (py_1) are late and overgrow previous phases. (C) Coarse-grained arsenopyrite
668 (coarse apy - assemblage II) overgrowing po_1+ccp_1. Fine-grained arsenopyrite (fine-apy -

669 assemblage III) occurs in microbands close to $pyrite_1$ pockets. (D) Sulfide-rich BIF with po_1+ccp_1
670 (assemblage I) overgrown by coarse-grained arsenopyrite (assemblage II). (E) Early po_1+ccp_1
671 (assemblage I) preferably grown in fold-hinges and small-scale shear zones overgrown by
672 brighter-colored po_2+ccp_2 (assemblage II), all phases are crosscut by a late veinlet containing
673 $pyrite_2$. (F) to (I) SEM imagens of thin sections from the Biquinho orebody. (F) ISS +
674 ccp_2+stilpnomelane (stp)+pyrite association. (G) pyrite and ISS at the borders of fine-grained
675 apy with fracture filled by native gold (Au), native bismuth (Bi) and po_2. (H) Gold inclusions in
676 fine-grained arsenopyrite surrounded by pyrite, po_2, stilpnomelane and carbonate (cb). (I) Gold
677 associated with pyrite bordered by quartz (qtz), po_2 and carbonate (cb). (J) Paragenetic table
678 showing relative timing of disseminated sulfide assemblages (I, II and III) and late veins – refer
679 to this table for relative timing and assemblage correlation. As-py – arsenian pyrite; sph –
680 sphalerite; Bi-sul – bismuth-sulfosalts; Bi-Te – bismuth tellurides.

681

682 **Figure 3:** $^{187}Re/^{188}Os$ vs. $^{187}Os/^{188}Os$ isochron plots: (A) for assemblage I pyrrhotite, and
683 assemblage II and III arsenopyrite and pyrite; (B) for assemblage I pyrrhotite; (C) assemblage II
684 arsenopyrite, (D) assemblage III arsenopyrite + pyrite, and (e) ^{187}Re-$^{187}Os^r$ isochron for
685 assemblage III sulfides. See text for discussion.

686

Figure 1_2 columns

Figure_2_1_page

Figure 2.
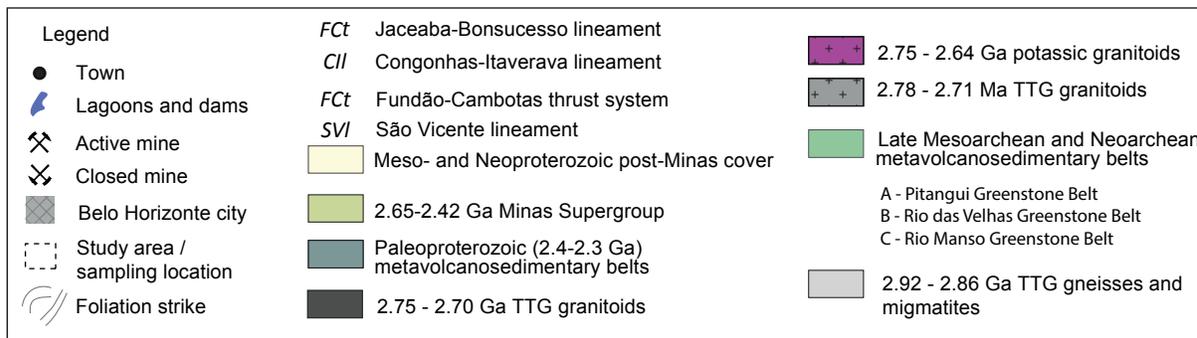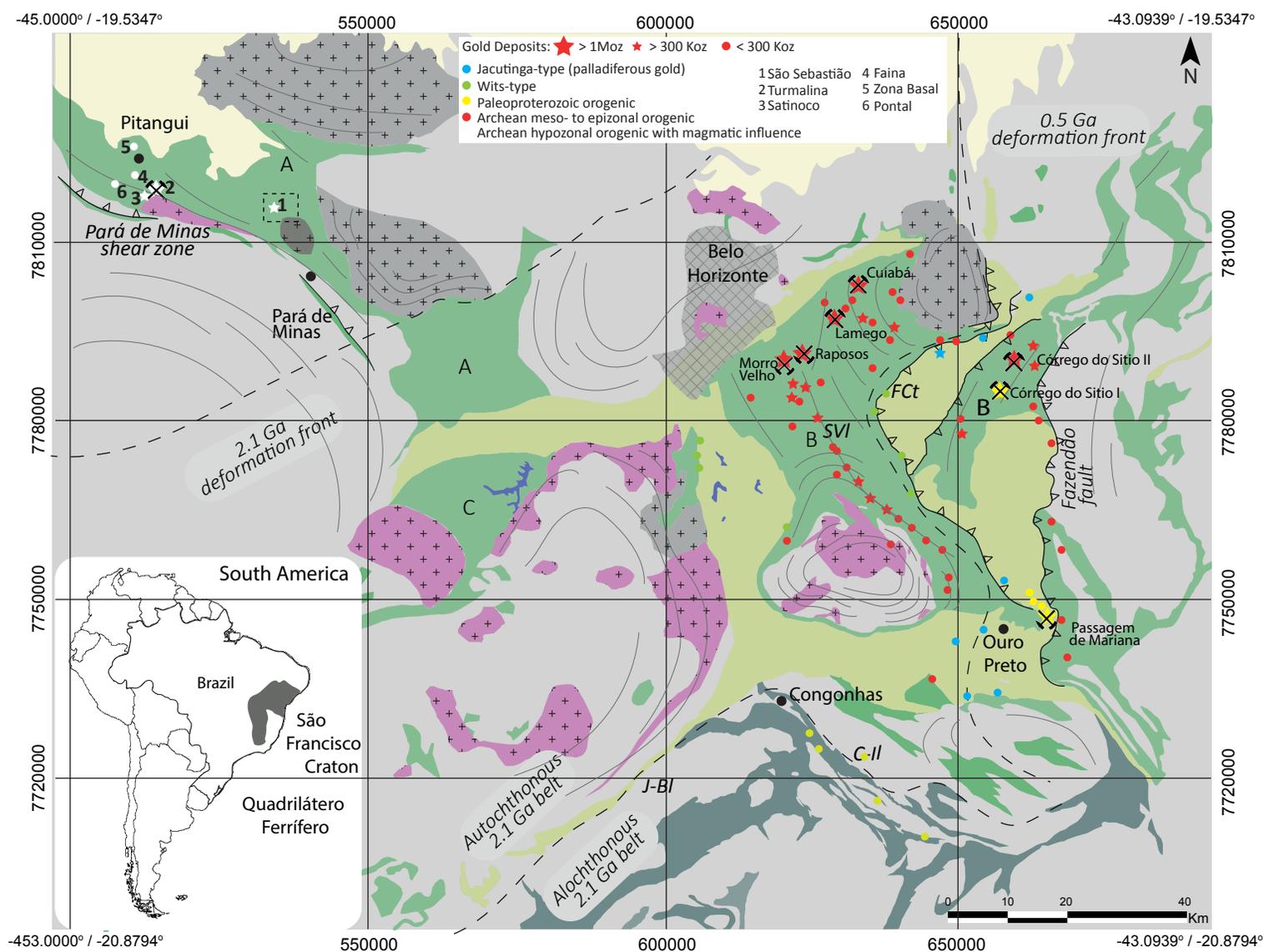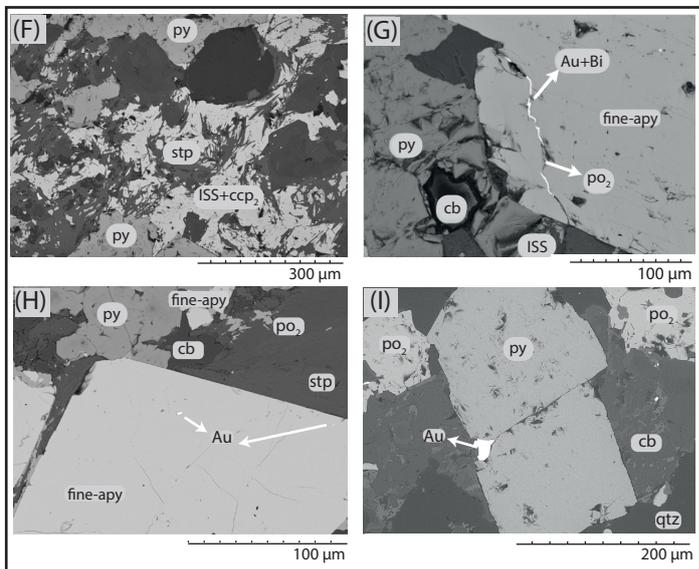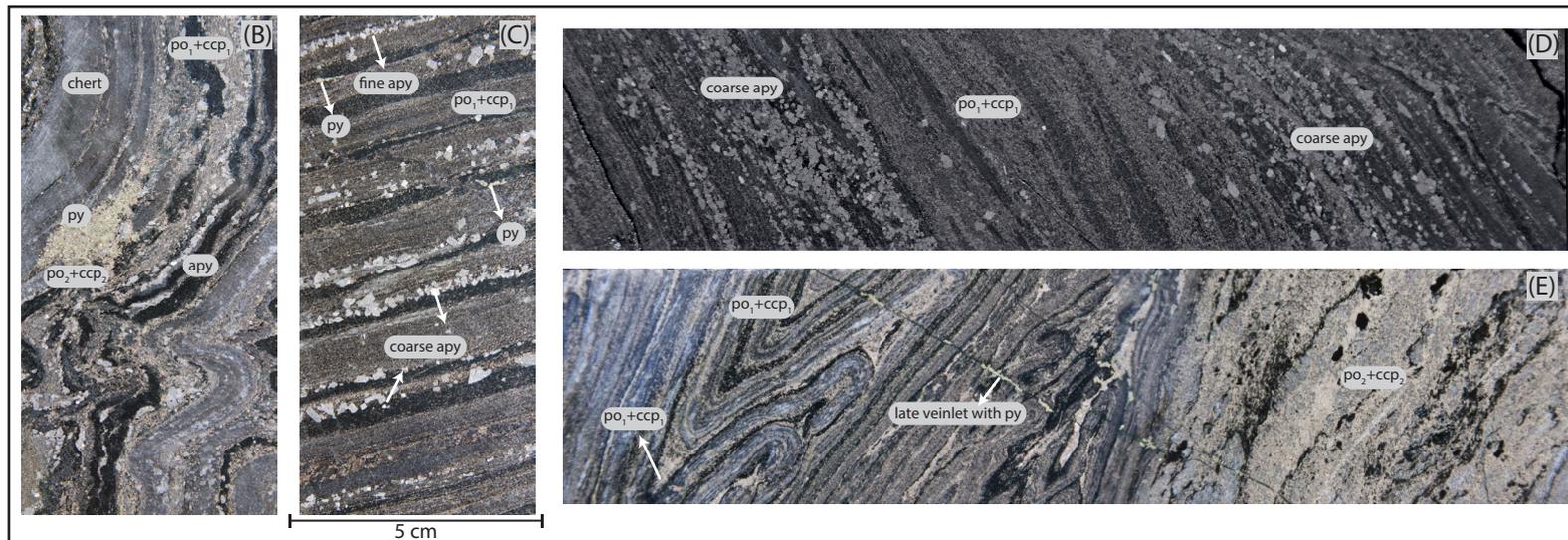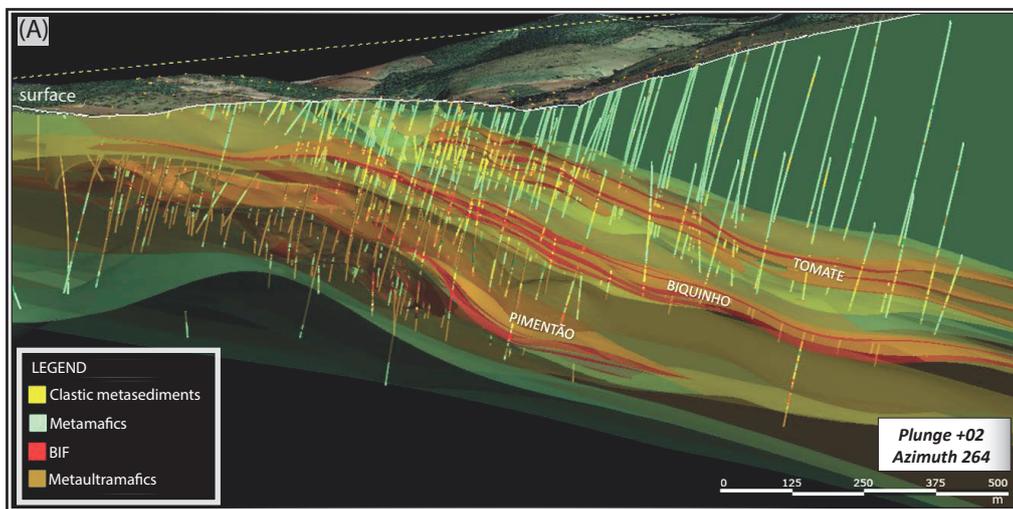
		Ore-related phases	Associated gangue	Texture	syn to post-D_n and D_{n+1} (Archean)	late high-T paragenesis	late veinlets
Sulfide assemblages	I	po_1 ccp_1	biotite chlorite prismatic Ti-magnetite quartz carbonate	. disseminated //S_n . filling saddle- reefs and fold hinges in BIF	▬▬ ▪▪▪ ▬▬ ▪▪▪		
	II	As-py coarse-apy	tourmaline grunerite hornblende, Fe-rich garnet	. disseminated, overgrowing S_n	▬▬▬ ▪▪▪▪		
	III	fine-apy ISS sph py_1 Bi-sul/ Bi-Te po_2 ccp_2 Au+Bi	stilpnomelane scheelite fluorapatite monazite anhedral Ti-magnetite coarse quartz carbonate	. growing over pyrrhotite$_1$ and chalcopyrite$_1$, . filling embaiments and fractures in previous phases . inclusions in previous sulfide phases, . disseminated in irregular patches, . disseminated in between the gangue, . filling fractures in apy(both) and py_1		▬▬▬ ▪▪▪ ▬▬▬ ▪▪▪ ▬▬▬ ▪▪ ▬▬▬ ▪ ▬▬▬ ▪▪▪ ▬▬▬▬ ▪▪▪▪ ▬▬▬ ▪▪▪	
		py_2 ccp_3	grunerite quartz carbonate	. late veins and veinlets			▬▪ ▬▪

Time

Figure 3_2 columns

a Assemblages I+II+III

$^{187}Os/^{188}Os$

$^{187}Re/^{188}Os$

Age = 2151 ± 86 Ma
initial $^{187}Os/^{188}Os$ = 0.1 ± 0.9
MSWD = 375
Isoplot Model 3

b Assemblage I

$^{187}Os/^{188}Os$

$^{187}Re/^{188}Os$

Age = 1989 ± 3900 Ma
initial $^{187}Os/^{188}Os$ = 0.1 ± 5.8
MSWD = 298
Isoplot Model 3

c Assemblage II

$^{187}Os/^{188}Os$

$^{187}Re/^{188}Os$

Age = 2187 ± 340 Ma
initial $^{187}Os/^{188}Os$ = -1.1 ± 5.3
MSWD = 224
Isoplot Model 3

d Assemblage III

$^{187}Os/^{188}Os$

$^{187}Re/^{188}Os$

IsoplotR Model 3
without #13
Age = 1987 ± 72 Ma
initial $^{187}Os/^{188}Os$ = 2.1 ± 0.7

Isoplot Model 3
All samples
Age = 2005 ± 980 Ma
initial $^{187}Os/^{188}Os$ = 2.2 ± 9.0
MSWD = 31
Without #13
Age = 1989 ± 347 Ma
initial $^{187}Os/^{188}Os$ = 2.1 ± 3.2
MSWD = 2.3

e Assemblage III

$^{187}Os^r$ (ppt)

^{187}Re (ppt)

Without #13
Age = 1988 ± 56 Ma
initial $^{187}Os^r$ = -0.1 ± 2.6 ppt
MSWD = 0.1
Isoplot Model 1

All samples
Age = 1998 ± 55 Ma
initial $^{187}Os^r$ = 0.0 ± 2.6 ppt
MSWD = 1.4
Isoplot Model 1

Table 1

Table 1. Synopsis of the Re-Os data for assemblage I, II, and III sulfides.

Name	Batch #	sample #	mineral	Grain size	Assemblage
RO1029-7_CCP1	RO1029-7	7	Pyrrhotite	fine	I
RO1108-2_2Po	RO1108-2	8	Pyrrhotite	fine	I
RO1108-3_3Po	RO1108-3	9	Pyrrhotite	fine	I
RO1108-7_7Po	RO1108-7	12	Pyrrhotite	fine	I
RO1029-1_APY1	RO1029-1	1	Arsenopyrite	coarse	II
RO1029-2_APY2	RO1029-2	2	Arsenopyrite	coarse	II
RO1029-3_APY3	RO1029-3	3	Arsenopyrite	coarse	II
RO1108-5_5Aspy	RO1108-5	11	Arsenopyrite	coarse	II
RO1029-4_APY4	RO1029-4	4	Arsenopyrite	fine	III
RO1029-5_APY+PY	RO1029-5	5	Arsenopyrite+pyrite	fine	III
RO1029-6_PY	RO1029-6	6	pyrite	coarse-fine	III
RO1108-4_4Aspy+Py	RO1108-4	10	Arsenopyrite+pyrite	fine	III
RO1108-8_Aspy	RO1108-8	13	Arsenopyrite	fine	III

Re (ppb)	±	Total Os (ppt)	±	^{187}Re (ppb)	±	^{192}Os (ppt)	±	^{187}Os^r (ppt) @ Osi = 0.12	^{187}Os^r (ppt) @ Osi = 0.5	^{187}Os^r (ppt) @ Osi = 1.0
0.984	0.004	73.8	1.0	0.618	0.002	20.5	0.4	24.2	21.8	18.5
0.258	0.001	17.8	0.1	0.162	0.001	5.3	0.0	4.9	4.2	3.4
0.238	0.001	25.5	0.1	0.150	0.001	8.4	0.1	5.2	4.2	2.8
0.264	0.001	19.9	0.1	0.166	0.001	6.2	0.0	4.9	4.1	3.2
13.413	0.047	391.7	2.3	8.431	0.030	40.2	0.2	294.3	289.5	283.1
13.629	0.047	383.5	2.3	8.566	0.030	38.5	0.2	290.3	285.7	279.6
12.281	0.054	415.5	2.2	7.719	0.034	55.3	0.2	281.7	275.1	266.4
7.311	0.025	191.9	2.1	4.595	0.016	10.0	0.1	167.7	166.5	164.9
11.014	0.038	369.1	2.1	6.923	0.024	44.8	0.2	260.8	255.4	248.3
9.713	0.037	301.7	1.8	6.105	0.023	31.7	0.1	224.9	221.1	216.1
2.260	0.008	75.2	0.8	1.421	0.005	9.0	0.1	53.4	52.3	50.9
8.361	0.029	271.9	3.2	5.255	0.018	30.6	0.3	197.9	194.2	189.3
4.944	0.017	165.9	2.0	3.107	0.011	18.3	0.2	121.7	119.5	116.6

$^{187}Os^r$ (ppt) @ Osi = 2.1	±	%$^{187}Os^r$ @ Osi = 0.12	%$^{187}Os^r$ @ Osi = 0.5	%$^{187}Os^r$ @ Osi = 1.0	%$^{187}Os^r$ @ Osi = 1.5	%$^{187}Os^r$ @ Osi = 2.1	$^{187}Re/^{188}Os$	±	$^{187}Os/^{188}Os$
11.4	2.7	96.7	86.9	74.0	61.1	45.6	95.5	2.1	3.87
1.6	0.7	95.8	83.2	66.8	50.3	30.5	96.3	1.0	3.03
-0.1	1.1	94.0	75.7	51.6	27.5	-1.3	56.4	0.5	2.07
1.0	0.8	95.2	80.7	61.6	42.6	19.8	84.9	0.8	2.62
1.0	8.0	99.5	97.8	95.7	93.5	91.0	663.2	3.8	23.27
269.1	7.8	99.5	97.9	95.8	93.7	91.2	704.3	4.0	23.99
266.2	9.0	99.2	96.9	93.8	90.8	87.1	442.1	2.8	16.26
247.2	5.1	99.8	99.0	98.1	97.2	96.0	1453.5	12.4	53.17
232.8	7.8	99.3	97.3	94.6	91.9	88.7	489.3	2.8	18.55
205.1	6.2	99.4	97.8	95.5	93.3	90.7	608.9	3.7	22.56
47.8	1.8	99.2	97.2	94.6	91.9	88.8	498.5	4.9	18.86
178.7	9.7	99.4	97.6	95.1	92.7	89.8	543.5	5.4	20.58
110.3	5.3	99.4	97.6	95.3	92.9	90.1	538.1	5.6	21.19

±	rho	% Re blank	%^{187}Os blank	%^{188}Os blank	Model age @Osi = 0.12	Model age @Osi = 0.5	Model age @Osi = 1.0	Model age @Osi = 1.5	Model age @Osi = 2.1	±
0.11	0.714	0.58	0.22	4.8	2308.7	2078.5	1774.2	1468.3	1099.2	255.2
0.03	0.767	2.90	0.28	3.7	1784.5	1554.1	1249.6	943.5	574.2	248.5
0.02	0.630	3.15	0.26	2.4	2043.0	1650.8	1130.7	606.0	-29.6	425.9
0.02	0.720	2.82	0.28	3.2	1740.8	1479.4	1133.6	785.8	365.8	282.1
0.15	0.569	0.04	0.02	2.5	2059.6	2026.4	1982.6	1938.8	1886.2	37.3
0.15	0.578	0.04	0.02	2.6	2000.5	1969.2	1927.9	1886.6	1837.1	35.2
0.10	0.504	0.05	0.02	1.8	2151.8	2102.0	2036.4	1970.8	1891.9	54.9
0.51	0.741	0.14	0.01	2.7	2151.7	2136.5	2116.6	2096.7	2072.7	21.6
0.12	0.572	0.05	0.02	2.2	2219.4	2174.5	2115.3	2056.1	1984.9	49.7
0.14	0.568	0.06	0.02	3.1	2171.8	2135.7	2088.1	2040.5	1983.3	40.7
0.21	0.788	0.31	0.13	12.2	2214.6	2170.4	2112.3	2054.2	1984.3	49.7
0.26	0.683	0.19	0.02	1.4	2218.3	2177.8	2124.5	2071.2	2007.2	48.2
0.28	0.701	0.29	0.01	1.0	2305.9	2265.0	2211.3	2157.5	2092.9	49.0
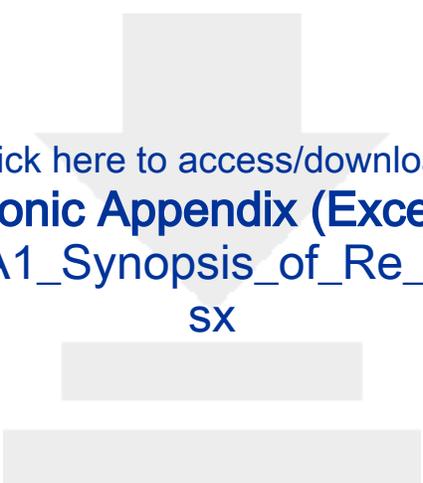
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Electronic Appendix (Excel etc.)
Appendix_Table_A1_Synopsis_of_Re_Os_data_FINAL.xlsx