

Fluid constraints for Au deposition at the *Monges* iron deposit, Ossa-Morena Zone (Montemor-o-Novo, Portugal)

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Abstract. The *Monges* deposit was an important iron mine during late 19th and early 20th century. In recent decades the region of Montemor-o-Novo has attracted the interest of several exploration companies due to high-grade gold anomalies found through soil geochemistry work. Exploration drilling carried out in the WNW-ESE and conjugated N-S shear-zones (≈30 km) identified interesting gold grades, including in the vicinity of the *Monges* iron deposit. The fluid inclusion study presented here is focused on constraining the fluids related to iron and gold mineralization processes. Fluid constraints for the iron mineralization are difficult to assess in the early stage (SEDEX environment) of the Ossa-Morena Zone geodynamic evolution. An overprinting of these early fluids is found, and most of the fluids present may be related to late metamorphism. Gold in *Monges* area shows affinity to a H₂O-CO₂-NaCl fluid system showing evidence of immiscibility and trace concentrations of CH₄. The geological settings hosting gold mineralization as well as the fluid characteristics with low-salinity, with an average of 7.72 wt. % NaCl Equiv. and homogenization temperatures between 150°C and 350°C, points towards an orogenic gold deposit model, corroborating and reinforcing the current accepted model for gold mineralization of Montemor-o-Novo region.

1 Introduction

The Ossa-Morena Zone (OMZ, Portugal) comprises a Fe-Zn metallogenic belt (Montemor-Ficalho) that hosts several Fe deposits with different recognized metallogenic origins, such as, 1) Fe-Skarn deposits related with Variscan igneous intrusions (Orada, Azenhas and Alvito deposits); and 2) massive iron ore deposits hosted in carbonate and calcsilicate rocks that are currently accepted to have formed in a SEDEX-VMS continuum which is the case of Montemor-o-Novo ancient mining complex (Salgueiro 2011, Salgueiro et al. 2011). *Monges* is part of the Montemor-o-Novo area composed of 10 iron ore mining sites and was the largest mine regarding its size and tonnage of iron ore exploited. The ore is mainly magnetite and the ore paragenesis is magnetite + pyrite + hematite + pyrrhotite (± chalcopyrite).

These mines ceased all exploitation in early 20th

century, more recently, gold anomalies were found through soil geochemistry, attracting exploration companies to the area. These companies carried out prospecting that revealed new data and interesting gold grades along a WNW-ESE shear zone (*Montemor-o-Novo* shear) which inflects to a N-S direction in the southeastern part of the shear belt (Ribeiro et al. 1993). This work aims to characterize the gold mineralization and its relationship with iron ore deposits that are spatially associated. Seven boreholes from the *Monges* area were sampled to characterize the fluids involved in the mineralization genesis; for this study samples from two boreholes were selected.

2 Geological setting

The Serra do Monfurado, where the Monges area is located, is characterized by three main geological formations (Araújo 1995; Chichorro 2006).

- i) Escoural Formation (Eldiacarian to Lower Cambrian) – characterized by black-schists with sparse intercalation of felsic rocks.
- ii) Monfurado Formation (Lower-Middle Cambrian) – a lower unit composed of felsic magmatic rocks (leptinites), and an upper unit of calcsilicate (skarn-like) rocks, marbles and dolomitic limestones;
- iii) Carvalhal Formation (Middle-Upper Cambrian) – mainly characterized by banded and massive amphibolites with N-MORB and E-MORB signatures.

2.1 Iron-oxide mineralization

In the *Monges* mine magnetite occurs as a massive ore (stratiform) and as disseminated mineralization in chloritic-amphibolitic marbles and calcsilicate rocks (skarn-like) from the Monfurado Formation (Salgueiro 2011 and references therein). Remobilization and reprecipitation has resulted in late cross-cutting vein structures and a magnetite + barite primary assemblage is commonly found in waste rock disposals.

2.2 Gold mineralization

Gold mineralization from Montemor-o-Novo developed within a late-Variscan WNW-ESE shear-zone, along a 30km belt which inflects to N-S direction in its most SE

zone, close to the Boa-Fé village (Ribeiro et al. 1993, Chichorro 2006, Inverno 2011). Gold mineralization is usually hosted in shear-zones affecting the Carvalho and Escoural Formations, where higher gold grades are found.

The main identified gold-bearing mineral assemblages are arsenopyrite, loellingite and pyrite, although hedleyite, native bismuth and maldonite were also found associated with quartz and calcite (São Pedro 2019, in prep.). These mineral assemblages are typically accompanied by intense hydrothermal alteration, such as sericitization and intense chloritization (propylitic alteration).

3 Fluid inclusions study

For this study eleven doubly polished thick sections were prepared ($\approx 200 \mu\text{m}$). Sampling was mainly focused in quartz (+ calcite) veins cross-cutting the host rocks. Over 300 individual fluid inclusions were studied using a LINKAM THMSG 600 microthermometry stage attached to a Nikon Eclipse 50Ipol with 100x long focus objective lens.

3.1 Fluid inclusion petrography

Fluid inclusions hosted in quartz, hornblende, tremolite and barite crystals were studied. Hornblende and tremolite were identified in late veins and in matrix alteration in felsic metavolcanic and calcsilicate (skarn-like) rocks from the Monfurado Formation. These minerals are interpreted to have formed during late metasomatic alteration of the host rocks in the shear zone.

Fluid inclusion petrography revealed two main FI types throughout all the studied samples, defined as Type I and Type II (Fig. 1 A-B).

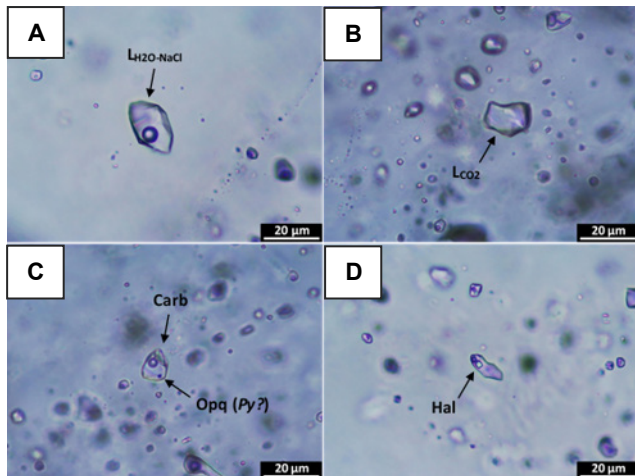


Figure 1. Examples of FI types from Monges samples where: **a.** Type I FI; **b.** Type II FI; **c.** Multisolid FI with an opaque (opq) and carbonate (carb) daughter mineral; **d.** Type I Halite-bearing FI.

Type I consists of two-phase fluid inclusions containing H₂O liquid and vapor phases. These FI show predominantly negative crystal shapes when related to primary fluid inclusion assemblages (FIA) and irregular

shapes in secondary FIA's, although this is not a necessary distinguishing factor between the two FIA's. Three phase NaCl oversaturated FIs were rarely identified in the studied samples, and are grouped in this type, containing H₂O liquid-rich and vapor phases and a halite crystal at room temperature ($\geq 25^\circ\text{C}$) (Fig. 1-D).

Type II fluid inclusions are characterized by two and three-phase FI's and were subdivided as Type II.a and Type II.b respectively. Type II.a FIs are multiphase having a CO₂-rich liquid phase plus an aqueous liquid phase. A CO₂ vapor phase may sometimes be present at temperature of 25°C. Type II.b consists of two phase inclusions with a CO₂-liquid phase and a CO₂ vapor phase.

Although these FI types are clearly predominant in the studied samples, it is important to note that CH₄ liquid-rich fluid inclusions occur with Type II FI cluster assemblages. Several inclusions from Type I and Type II were identified as containing one or two solid phases in their composition, sometimes with an opaque daughter mineral (Fig. 1.C).

3.2 Microthermometry data

Figure 2 plots Salinity (wt. % NaCl Equiv.) versus Th, displaying the microthermometry results of all the FI's studied, arranged by host mineral.

Type I FI's eutectic temperatures (T_e) range between -10.2°C and -49.4°C , corresponding to fluids with several solutes in its composition, such as, NaCl, MgCl and CaCl₂. Salinities were calculated from ice melting temperatures ($T_{m\text{ice}}$), ranging from 0.88 and 23.18 wt. % NaCl Equiv. with a mean of 7.72. Homogenization temperatures (T_h) were measured between 116°C and 460°C, with a T_h average of 253°C. There were decrepitation temperatures (T_d) measured between 216°C and 247°C. Type I FI data includes the FI's where one or two daughter mineral phases were found, with higher salinities - ranging from 32.9 to 34.7 wt. % NaCl Equiv. (calculated from halite melting temperature, $T_{m\text{Hal}}$) and T_h values of 116°C, where vapor homogenized into liquid and $T_h < T_{m\text{Hal}}$.

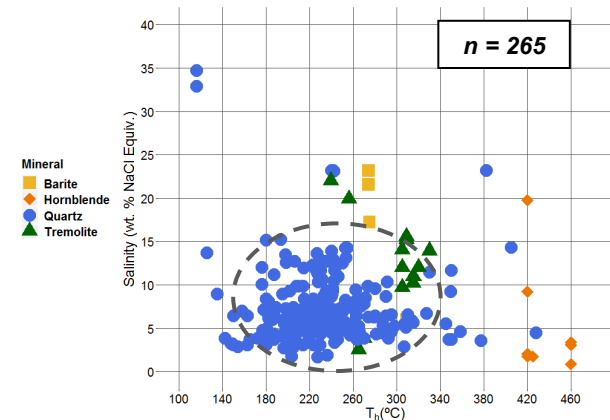


Figure 2. Salinity (wt. % NaCl Equiv.) versus T_h , for Type I FI, organized by host mineral. The dashed line represents 95% of the data.

Type II FIs were studied exclusively in quartz crystals and subdivided into Type II.a and Type II.b due to their different compositions. Type II.a FIs revealed CO₂ melting temperatures (T_{mCO₂}) ranging from -58.6°C and -56.8°C, with corresponding CO₂ homogenizations (Th_{CO₂}) between +3.9°C and +24.6°C. Salinities range from 7.17 and 18.04 wt. % NaCl Equiv.

Type II.b shows liquid CO₂ as their dominant component, and T_{mCO₂} range from -57.5°C and -56.8°C. Th_{CO₂} were measured from 0°C and 5°C.

3.3 Raman spectroscopy

Raman spectroscopy was carried out on the main FI types aiming to identify the volatiles and solids observed in FIs during petrography and microthermometry studies.

Figure 3-A shows a barite typical Raman spectrum with its characteristic main Raman vibrations at 986 cm⁻¹ (v1), 458 cm⁻¹ (v2), 1141 cm⁻¹ (v3), 615 cm⁻¹ (v4), which allowed for the identification of the host mineral of some of the studied FIs.

The solids present in Type I FIs were studied by this technique allowing the identification of calcite as the main daughter mineral phase (1084 cm⁻¹) (Figure 3-B). The opaque daughter mineral found in some FI's could not be identified due to its small size (≈ 1 μm).

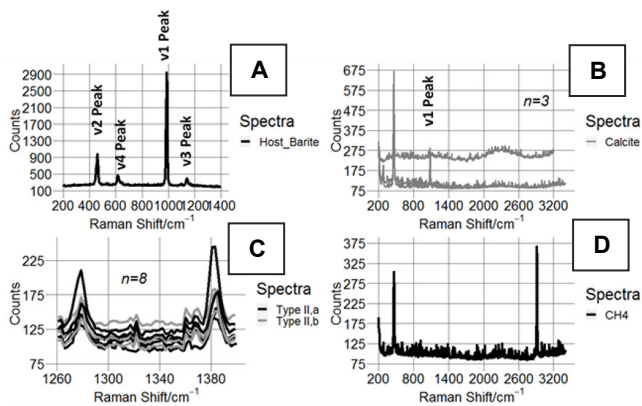


Figure 3. Collected Raman spectra for FIs. **a.** Barite host mineral. **b.** Calcite identification with main Raman vibration of 1084 cm⁻¹. **c.** Raman spectrum from liquid CO₂ analysis of Type II subtypes. **d.** Raman spectrum example of liquid CH₄.

Liquid CO₂ was identified in Type II (Type II.a and Type II.b) FIs by its characteristic Raman main vibrations of 1285 cm⁻¹ and 1388 cm⁻¹ (Fermi doublet). The obtained spectra allow for the calculation of the Fermi Diad distance (Δ), in order to determine the CO₂ density (g/cm³) for these types of FIs. Figure 3-C shows some of the obtained spectra for Type II.a and Type II.b FIs. Fermi Diad distance of Type II.a range from 104.25Δ and 107.22Δ with an average of 105.75 Δ corresponding to a CO₂ density of 1.2 g/cm³. Type II.b FIs showed Fermi Diad distances between 104.25 and 106.52Δ with an average of 105.00Δ, which corresponds to CO₂ densities of 0.92 g/cm³. The average values between these two subtypes of Type II FI's reveal a 105.38Δ distance indicating a CO₂ density of 1.06 g/cm³. Although their scarcity, several CH₄-

bearing fluid inclusions were identified and studied, Raman spectroscopy shows that these FI's composition is near a pure CH₄ composition (Fig. 3-D).

4 Fluid flow contribution for mineralization

The gathered FI data reflects the fluid circulation in the Montemor-o-Novo shear zone affecting the Escoural, Monfurado and Carvalhal Formations, where gold-mineralization occurs. This puts aside the possibility that the studied fluids are related to the iron mineralization of the Monges deposit, which precedes the gold-related mineralizing events. Primary fluids were most certainly overprinted by late-metamorphic fluids as can be evidenced by the FI present in the amphibole group minerals. Therefore, the data gathered in this study concerns mainly the late episodes related to the gold ore genesis. This study provides evidence for a revised metallogenic model for gold emplacement for the Ossa-Morena Zone.

Previous studies classify the Montemor-o-Novo deposit as an orogenic gold related deposit (Ribeiro et al. 1993, Pereira et al. 2002, Inverno, 2011). The metallogenic models have been supported by regional structural studies and hydrothermal alteration geochemistry, although, no fluid inclusion studies were ever carried out. The work presented herein is the first FI study elucidating gold transport and deposition in the Montemor-o-Novo gold deposit.

The iron and gold mineralizations although being in the proximity of one another, clearly show different genetic and metallogenic evolutions.

4.1 New Research

The relatively low salinity fluids (< 10 wt. % NaCl Equiv.) and T_h temperatures between 150°C and 350°C are consistent with typical fluid properties identified for orogenic gold deposits worldwide (Bodnar et al. 2014).

The T_e (first ice melting temperatures) range indicates the presence of Mg²⁺ and Ca²⁺ in the fluids trapped in Type I FIs (Fig. 4). The presence of these ions justifies the crystallization of calcite daughter minerals in some of the studied FIs.

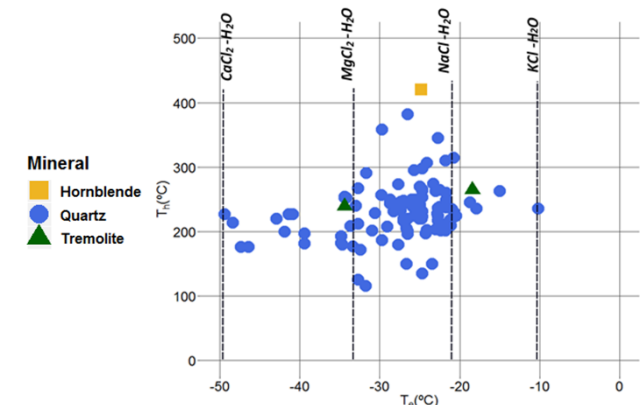


Figure 4. Th versus Te plot showing the solutes content in the different types of FI's. Content estimated from first ice melting temperatures.

The higher T_h values found in Type I FIs were recorded in metamorphic amphiboles (hornblende and tremolite) indicating that metamorphic fluids reached temperatures of 460°C, close to metamorphic peak conditions described for the region (Pereira et al. 2012).

Type II CO₂-bearing fluid inclusions in assemblages with Type I FIs indicated a H₂O-CO₂-NaCl system. The different H₂O and CO₂ concentrations suggest that immiscibility occurred, reflecting devolatilization of the amphibolite and black-schist units. Halite bearing fluid inclusions are rare (two FIs registered) and are not representative of the mineralizing fluids (Robert et al 1995; Boullier et al. 1998).

CH₄ concentrations in H₂O-CO₂-NaCl and CO₂-pure FIs is estimated to be ≈ 5 mol. % (Fig. 5). Nevertheless, liquid CH₄ bearing FIs were found in samples from quartz veins that cross-cut carbonate/calcsilicate host rocks and could be evidence of organic matter thermal degradation in these lithologies (Demir et al. 2017).

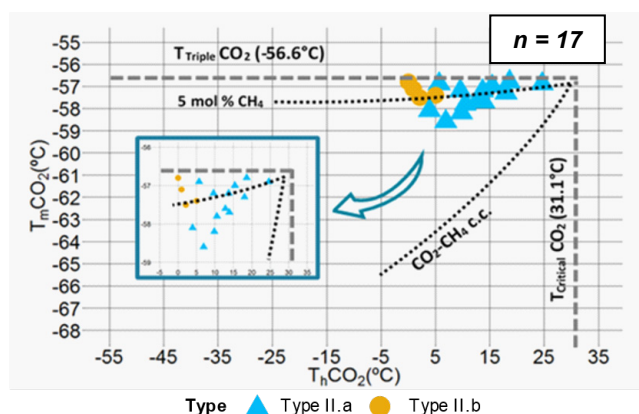


Figure 5. T_{mCO_2} versus T_{hCO_2} plot from CO₂-bearing fluid inclusions. Trend lines adapted from Bodnar et al. (2014).

5 Conclusions

Data suggests that gold mineralization originated from low to medium salinity fluids in a H₂O-CO₂-NaCl system, containing variable concentrations of CO₂ in their composition. This indicates that immiscibility occurred, possibly due to fluid pressure cycles promoted by cyclical reactivation of the host shear zones in ductile and brittle regimes (Ribeiro et al. 1993). Fluid temperatures ranged from 150°C to 350°C, although during peak metamorphism they could be higher than 460°C, as seen in FIs hosted by amphibole.

The data corroborates the orogenic gold model accepted for this deposit, although, identifying a clear source for the gold-bearing fluids is unresolved. The data presented here closely approaches a model where fluids may have had a high metamorphic devolatilization contribution generated by the Montemor-o-Novo WNW-ESE and N-S Boa-Fé shears.

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