

## FLUID COMPOSITION IN ORTOSA Au-SKARN AND EL VALLE-BOINÁS Cu-Au SKARN, RÍO NARCEA GOLD BELT (SPAIN).

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The Río Narcea Gold belt (Spiering et al., 2000) is the most explored and prolific gold-producing belt in NW Spain. The belt is spread out along a narrow NE-SW band of about 45 Km in width and consists of several longitudinal folds affecting Palaeozoic sediments crosscut by a fracture net. Granitoid emplacements are related to the fractures. Some of these granitoids produced skarn mineralizations. At present, the best known skarns are those related to the Carlés, Boinás and Ortosa intrusions, (Martin-Izard et al., 2000; Cepedal et al., 2000; Fuertes-Fuente et al., 2000). These skarns have clear differences in the geochemistry of igneous rocks to which they are related, in their host-rocks and skarn mineralogy.

This paper focuses on the skarns of the Boinás and Ortosa intrusions. In the first case, calcic and magnesian Cu-Au skarns with economic interest were developed. The El Valle-Boinás deposit is currently being mined for gold at a planned rate of 125,000 oz/y. In the second case, a reduced Au skarn was developed, which is still under exploration. In this paper we present the results from microthermometry and Raman analyses performed on fluid inclusions from these skarns. The objective of this study is to know the composition of skarn-related and ore fluids that allow us to compare the conditions of formation of these two gold deposits.

### Fluid inclusions description

**Aqueous-carbonic inclusions [L(V)c-w (CO<sub>2</sub>)]:** These inclusions have been found in quartz from veins in the Ortosa and Boinás intrusions. These veins consist of quartz, calcite and sulphides, and developed sericitic alteration of the igneous rocks. Sulphides are mainly arsenopyrite and pyrite at Boinás and arsenopyrite, löllingite, pyrrhotite and pyrite at Ortosa. The inclusions occur isolated or in small clusters, and are classified as primary. Their microthermometric characteristics and Raman data are in table 1.

**CH<sub>4</sub>-bearing inclusions:** This group of inclusions comprises two types: aqueous-methane inclusions [L(V)c-w(CH<sub>4</sub>)] and monophasic methane inclusions (Vc). The first type has only been found at El Valle-Boinás deposit until now. These inclusions occur in quartz veins from early retrograde magnesian skarn. They consist of a methane-rich bubble (from 20 to 80%), an aqueous phase and a small opaque mineral (around 0.1%). Sometimes, a prismatic solid with high-relief and a moderate birefringence was also observed. They are considered as primary.

The second type, (Vc), was found in both skarns. At El Valle-Boinás, the inclusions occur in association with the aqueous-methane inclusion described above, but they are scarce and distributed in groups and were also considered as primary. At Ortosa, these inclusions also occur in quartz from retrograde skarn. In this case, the inclusions are aligned along small fractures that never crosscut more than one crystal, so they were considered as pseudosecondary. Their microthermometric characteristics and Raman data are in table 1.

**Multiphase inclusions:** These inclusions consist of a bubble that occupies between 2 and 10% of the inclusion, an aqueous phase and several solid minerals (Fig. 1). The beginning of ice melting occurs between -75 and -70 °C, indicating the presence of a complex mix of salts such as NaCl, CaCl<sub>2</sub>, KCl, MgCl<sub>2</sub>, LiCl, etc... They were considered as primary.

At El Valle-Boinás these inclusions occur in quartz veins related to early retrograde magnesian skarn. These inclusions are isolated or in groups of two or three. The T<sub>m,ice</sub> ranges from -44.5 to -31.0 °C. T<sub>m</sub> of halite and sylvite ranges from 306 to 425 °C, and from 80 to 100 °C respectively. Homogenization temperatures range from 343 to 520 °C in liquid (Cepedal et al., 2000). At Ortosa these inclusions occur in quartz of early retrograde skarn. In these inclusions only T<sub>m</sub> halite was obtained (around 255 °C), and the T<sub>h</sub> was not reached because of the inclusions decrepited close to 450 °C (Fernández et al., 2001).

This type of inclusion shows a similar number and type of included solid minerals in both skarns. All the inclusions show a halite cube (from 2 to 10%). A sylvite crystal (around 5%) also occurs in some inclusions. Moreover, other different solids have been observed in some inclusions: a prismatic mineral similar to that described above (from 5 to 10%), an irregular and small solid with high-relief and high birefringence (up to 3%) that could be a carbonate, and a small opaque mineral (around 0.1%) similar to that described above. Identification of sylvite and halite was carried out by the melting temperatures and optical properties. In some cases the opaque mineral has a bigger size with a triangular cross-section, and may be chalcopyrite.

### Raman data

Some inclusions of these typologies were selected for analysing by Raman spectroscopy. The analyses were carried out in order to identify volatile species and solids.

**Volatile phase:** Raman analyses confirm the presence of other volatile phases in addition to CH<sub>4</sub> and CO<sub>2</sub>, showing compositional differences between inclusions of the same type from both skarns. Raman data are in Table 1.

Raman analyses of aqueous-carbonic inclusion from Boinás confirm the pure CO<sub>2</sub> composition of the volatile phase. Aqueous-carbonic inclusions from Ortosa also have a volatile phase dominated by CO<sub>2</sub>. But in this case there are significant

quantities of CH<sub>4</sub> (0.9 to 6.0%), N<sub>2</sub> (3.0 to 4.0%) and H<sub>2</sub>S (0.1 to 0.3%). This could indicate more reduced conditions in the alteration of the Ortosa granitoid.

The aqueous methane inclusions from Boinás show a volatile phase dominated by CH<sub>4</sub>, and have variable quantities of other components such as CO<sub>2</sub> (0.83 to 4.5%), N<sub>2</sub> (1.0 to 2.0%), H<sub>2</sub>S (0.7%) and C<sub>2</sub>H<sub>6</sub> (≈0.07%).

Monophase-methane inclusions from Boinás also have a volatile phase dominated by CH<sub>4</sub>, with variable quantities of CO<sub>2</sub> (0.0 to 3.0%), N<sub>2</sub> (0.3 to 33.0%) and C<sub>2</sub>H<sub>6</sub> (≈0.07%). In this case there is an important variation in the N<sub>2</sub> proportion. The inclusions that do not contain N<sub>2</sub> have CO<sub>2</sub> instead. This heterogeneous composition could explain the presence of different temperatures of ThCH<sub>4</sub> in critical state. This type of inclusions from Ortosa has, however, a volatile phase dominated by N<sub>2</sub> and very homogeneous compositions (25.0 to 26.0% CH<sub>4</sub>, 74.0 to 75.0% N<sub>2</sub>), as has already been pointed out during microthermometric study. C<sub>2</sub>H<sub>6</sub> was not detected.

**Daughter minerals:** Raman microprobe analysis at El Valle-Boinás and Ortosa allowed us to identify the prismatic mineral as pyrosmalite [(Fe,Mn)<sub>8</sub>Si<sub>6</sub>O<sub>15</sub>(OH,Cl)<sub>10</sub>] (Fig. 2) and the high-birefringence mineral as calcite. The presence of chalcopyrite could not be confirmed due to the fact that this mineral seems to melt under the laser beam.

Pyrosmalite has been previously identified as a daughter mineral in multiphase fluid inclusions from several Cu-Au-Co and Pb-Zn-Ag deposits in the Cloncurry district, Australia (Dong and Pollard, 1997). Pyrosmalite is also a common retrograde hydrothermal phase in these deposits. However, the presence of this mineral as a alteration phase at El Valle-Boinás and Ortosa skarns has not yet been confirmed.

Type		ThCH <sub>4</sub> (°C)	TmCO <sub>2</sub> (°C)	ThCO <sub>2</sub> (°C)	Tmhyd (°C)	Th (°C)	XCO <sub>2</sub> (%)	XCH <sub>4</sub> (%)	XN <sub>2</sub> (%)	XH <sub>2</sub> S (%)
L(V)c-w (CO <sub>2</sub> )	Boinás		-57 to -56,6	30 to 31.5	8,4 a 9,4	385 to 405 G 358 to 378 C 225 to 345 L	100	0	0	0
	Ortosa		-58.5 to -56.6	17.5 to 28.3	7.5 to 10.9	310 to 420 G	89.7 to 95	0.9 to 6	3.0 to 4.0	0.1 to 0.3
L(V)c-w (CH <sub>4</sub> )	Boinás	-100.5 to -82.5 G -84 L -88.5 to -83.4 C			13 to 18.3	365 to 433 G 378 to 387 L 380 C	0 to 4.5	93.8 to 100	0 to 2	0 to 0.7
	Vc	-105 to -98.8 G -84 to -83 L -82.9 to -82.2 C -99.0 C					0 to 3	67 to 97.4	0.3 to 33	0
	Ortosa	-133.5 to -128 G					0	25 to 26	74 to 75	0

Table 1. Summary of microthermometric (Cepedal et al., 2000; Fernández et al., 2001) and Raman data of volatile bearing inclusions.

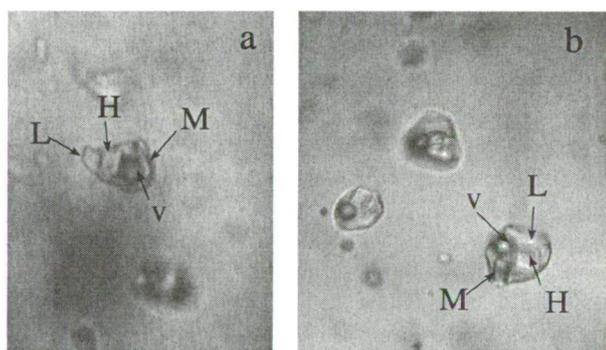


Fig. 1. Photo of multiphase fluid inclusions from Ortosa (a) and Boinás (b). v: vapour, L liquid, H: halite, M: pyrosmalite. Size of inclusions is around 15µm.

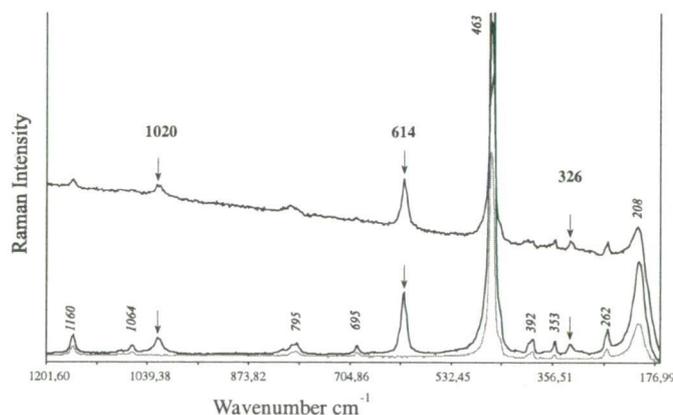


Fig. 2. Raman spectrum (black) of the prismatic daughter mineral in the multiphase inclusions from Ortosa (a) and Boinás (b), showing the mean peak of pyrosmalite. Spectrum in grey is of quartz form matrix.

## References

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