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FLUID INCLUSIONS, STABLE ISOTOPE, AND GEOCHRONOLOGICAL CONSTRAINTS ON THE ORIGIN OF THE NAMBIJA OXIDIZED GOLD SKARNS (ECUADOR)

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Introduction

The Nambija gold district is located in the sub-Andean zone of southeastern Ecuador, 40 km from the Peruvian border. The district is the main gold producer of Ecuador, together with the gold-silver epithermal district of Portovelo-Zaruma. Total resources were estimated at 125 to 155 metric tons Au and the production since 1980 estimated at 60-90 metric tons Au (Prodeminca, 2000).

The gold deposits occur within and close to skarn bodies developed on volcano-sedimentary rocks of the Triassic Piuntza Unit. Gold grades are typically high (up to 150 g/t) whereas the contents in Cu, Zn, Pb and other metals are in most deposits very low. Different genetic models have been evoked for the Nambija mineralization. According to Litherland et al. (1994) and Prodeminca (2000), the Piuntza Unit has been contact-metamorphosed and skarnified by the Zamora intrusion and gold is the result of a later epithermal event. Alternatively, a magmatic-hydrothermal model of oxidized gold skarn is proposed by Hammarstrom, (1992), Meinert (2000), Fontboté et al. (2004), and Markowski et al. (2006).

We present here geological, mineralogical, fluid inclusion, stable isotope analysis and preliminary age determinations. We then propose a genetic model for the formation of the Nambija oxidized gold skarns. Detailed descriptions of skarn and mineralization can be found in Fontboté et al. (2004) and Markowski et al. (2006).

Geological setting and ore mineralogy

The Nambija district gold skarn deposits are hosted by the Triassic Piuntza volcanosedimentary unit (Litherland et al. 1994). Subduction related magmatism occurred in the Jurassic with intrusion of the Zamora batholith and deposition of the related Misahuallí volcanoclastic formation. Rifting during Early Cretaceous led to deposition of the marine Hollín Formation. The sub-Andean zone was uplifted during Late Cretaceous to Paleocene (Jaillard et al. 2005; Pratt et al. 2005).

The Nambija oxidized gold skarns developed mainly in volcanoclastic rocks of the Piuntza unit, which occurs as a 20-km long, north-trending, contact-metamorphosed lens within the Jurassic Zamora batholith. The skarn bodies are spatially associated with porphyritic intrusions cutting the Zamora batholith and the Piuntza unit. From observations carried out at Fortuna and Campanillas it is inferred that the transition from the exoskarn (in the Piuntza unit) to the associated porphyritic intrusions occurs through the broadly contemporaneous development, in the porphyritic intrusions, of an outer endoskarn zone (Na-rich plagioclase, actinolite, diopside, K-feldspar and/or titanite) and an inner pervasive and B vein-controlled potassic alteration zone (K-feldspar > biotite and/or magnetite and/or titanite). A K- and Na-metasomatic zone is developed on the outer margin of the exoskarn within volcanoclastic rocks of the host Piuntza unit.

The exoskarn is predominantly made up of massive brown garnet (mean Ad₅₅). Subordinate pyroxene-epidote skarn developed mainly at the margins of brown garnet skarn bodies. Mostly idiomorphic garnet (mean Ad₅₅) occurs in blue-green skarn formed as a later phase, in places with high porosity, at the transition with vugs and discontinuous dilational type I veins. The last garnet generations are mainly andraditic and generally occur as honey-yellow clusters and crosscutting bands (mean Ad₈₄). As is typical for other skarns developed in volcanoclastic rocks, the zoned mineralogy is poorly defined.

Gold deposition is related to the weak retrograde stage and preferentially occurs in vugs and type I veins (vein nomenclature in Fontboté et al., 2004) filled, in order of decreasing abundance, by buck quartz, K-feldspar, ±calcite, ±chlorite, ±epidote, ±plagioclase ±muscovite and, in places, by subordinate pyrite, hematite, sphalerite, and chalcopyrite. Gold was observed in type II veins but not in sulfide-rich type III veins, which crosscut the previous veins. It occurs within buck quartz in vugs and type I veins and was never observed within later comb quartz. Some gold occupies an interstitial position between garnet and pyroxene grains in skarn affected by retrograde alteration but lacking vugs and veins, as frequently observed in blue-green garnet skarn. Metal and sulfur contents are low at Fortuna and the highest gold grades coincide with high hematite abundance.

Fluid inclusion study

Fluid inclusions have been observed in garnet, pyroxene, quartz, and calcite from gold-bearing veins, magmatic quartz from the Fortuna and Campanillas-Katy intrusions, quartz from the B veins cutting the Fortuna intrusion, and post-ore calcite. Results are shown in Fig. 1

High temperature – high salinity fluids (321° to >600°C and 30.9 to 65.6 wt% eq NaCl) are recorded as primary fluid inclusions (*type Lh*) in pyroxene from the green pyroxene-epidote skarn and from the endoskarn, in magmatic quartz from the Fortuna and Campanillas-Katy intrusion, and in quartz from B vein cutting the Fortuna intrusion. In magmatic quartz, in quartz from B vein, and in pyroxene from endoskarn they often occur in spatial association with vapor-rich Lc and/or L1 fluid inclusion suggesting boiling assemblage.

Aqueous carbonic fluids (*type Lc*) are recorded in magmatic quartz from the Fortuna and Campanillas-Katy intrusion, in quartz from B vein cutting the Fortuna intrusion, and in pyroxene from the endoskarn. They occur also in blue-green skarn garnet and in quartz from vugs and type I vein. Raman spectrometric analyses indicate presence of CO₂ and N₂, with a CO₂ content between 94 and 100 mol%. H₂S was identified in about one third of the inclusions. Carbon dioxide bulk content ranges from 55 to 1.6 mol%, N₂ content ranges from 1.3 to 0 mol%, and salinity is between 20 and 1.9 wt% eq NaCl. They homogenize to liquid, critical or vapor phase between 565° and 294°C. Type Lc fluid inclusion from the magmatic quartz are strongly affected by necking down and show a large variation of densities and CO₂ content.

Aqueous fluid inclusions homogenizing to vapor (L1) display homogenization temperatures between 513° and 341°C and salinities from 17.4 to 1 wt% eq NaCl. They were recorded as primary fluid inclusions in pyroxene from endoskarn and in late garnet and epidote from clusters and blue-green skarn. They were also recorded in gold-bearing quartz from vugs and type I veins where they are in spatial association with part of the L2 and Lc fluid inclusions. The highest homogenization temperature and salinities were encountered in garnet of the blue-green skarn.

Aqueous fluid inclusions homogenizing to liquid (L2) occur in magmatic quartz, in B vein quartz, in late garnet and epidote from clusters and blue-green skarn, and in the quartz from vugs and type I veins. Two of them were observed in pyroxene from the green pyroxene-epidote skarn. They are primary in the two garnet type and in epidote. Part of them are spatially associated with L1 and Lc fluid inclusions in quartz from vugs and type I veins but other occur as isolated inclusions. They homogenize to the liquid phase between 455° and 318°C. The highest salinities were found in inclusions within garnet and epidote of the blue-green garnet skarn and in pyroxene. Type L2 fluid inclusions from the late garnet cluster, quartz and epidote from vugs and type I veins show similar homogenization temperatures and salinities (Fig. 5). Type L2 fluid inclusions show similar salinities and homogenization temperatures as L1 and Lc type when spatially associated.

Fluid inclusions with Th <302°C (*type L3(h)*) are the most abundant and were observed in magmatic quartz, quartz and calcite of vugs and type I veins and in calcite sealing post ore normal

faults. They occur as secondary fluid inclusion in magmatic quartz and quartz of vugs and type I veins. They are primary in clear comb quartz of type I veins and in calcite from vugs, type I veins, and post-ore normal faults. Salinities range from 25.2 to 0.2 wt% eq CaCl_2 . They homogenize to liquid in the range $302^\circ\text{-}74.5^\circ\text{C}$ with the lowest Th and high salinities typically found in post-ore calcite. Type L3h homogenize by halite dissolution. Calculated salinities are between 30.8 and >50 wt% eq NaCl as some L3h fluid inclusions decrepitate at 420°C before total halite dissolution. They are interpreted as being the result of post-trapping modifications.

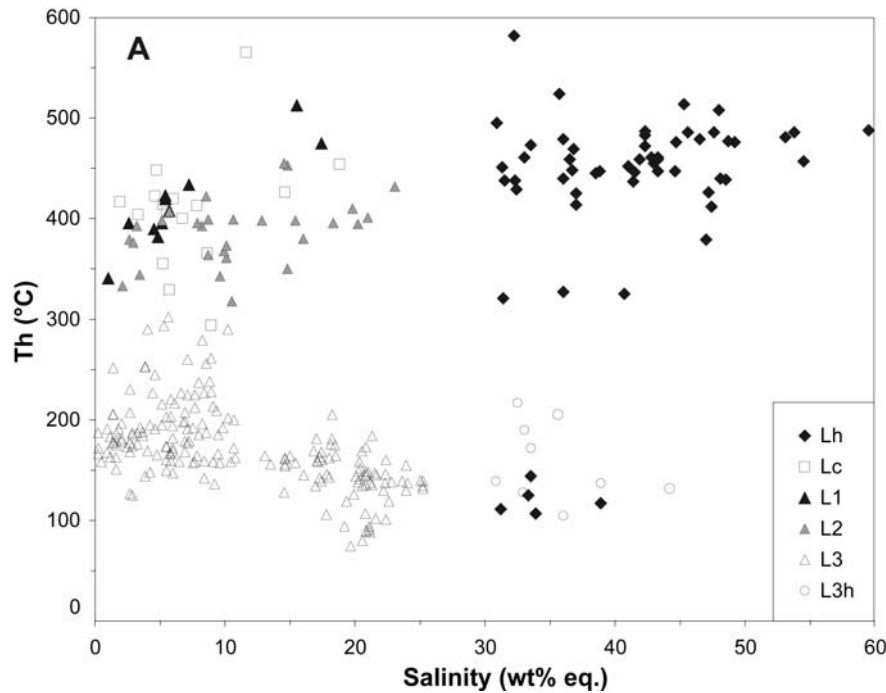


Fig. 1 Binary plots of temperature of bubble or vapor disappearance (Th) vs. Salinity with data ordered by fluid inclusions type

Stable isotope compositions

Oxygen isotope compositions were measured for milky quartz and post gold comb quartz from vug and type I veins, and on quartz from type III veins. Carbon and oxygen isotope composition were also measured for calcite from vug and post ore veins.

Calculated $\delta^{18}\text{O}_{\text{water}}$ values in equilibrium with milky, comb and type III vein quartz are between 4.6 to 10.8‰, -3.7 to 0.6‰, and 0.4 to 5.9‰, respectively. Calcite from vugs and post-ore stage has $\delta^{18}\text{O}$ values of 7.6 to 6.8‰ and 15 to 14.6‰, respectively. Calcite from vugs and post-ore stage has similar $\delta^{13}\text{C}$ values of -8.6 to -10‰ and -8.3 to -8.4‰ respectively, compatible with an igneous source for carbon. The calculated $\delta^{18}\text{O}_{\text{water}}$ values of calcite from vugs ($250^\circ\text{-}350^\circ\text{C}$) and post ore stage ($120^\circ\text{-}160^\circ\text{C}$) range from -0.7 to 2.5‰ and -1.2 to 2.7‰, respectively.

Skarn and mineralization ages

Titanite from the Fortuna endoskarn were separated at the University of Geneva and four preliminary analyses yielded a U-Pb concordia age of 145.65 ± 0.52 Ma. Molybdenite from two post-gold type III vein samples of the Nambija - El Tierrero mine were separated at AIRIE in Colorado and yielded Re-Os ages of 145.92 ± 0.46 Ma and 145.58 ± 0.45 Ma. Maximum U-Pb age and minimum Re-Os ages for gold deposition are indistinguishable setting gold deposition at 145.72 ± 0.27 (MSWD = 0.61)

Conclusions

We interpret the Nambija skarn formation and gold deposition as being related to the intrusion of felsic bodies at ca. 145.5Ma. Fluids exsolved during crystallization of these intrusions are responsible

for potassic alteration grading into skarnification. Limestone and/or carbonate-rich and/or more permeable levels were selectively replaced by an oxidized skarn assemblage while less reactive and/or less permeable lithologies suffered mostly Na- and K-metasomatism giving the bedding-parallel form of most skarn bodies.

The coexistence of high-salinity fluids and low-salinity CO₂-bearing fluids is interpreted to result from boiling of a magmatic fluid of moderate salinity. Isochore modelling of a 11wt% eq NaCl and 7 mol% CO₂ Lc fluid inclusion homogenizing at 565°C to the vapor phase, suggests pressure in excess of 120-140 MPa i.e. 5-6 km depth. Cooling of the system at constant pressure/depth prevented further boiling during type I vein formation at the brittle/ductile transition around 400°C, providing a single aqueous carbonic fluid of magmatic origin. The oxidizing conditions at this stage (hematite stable) preclude gold transport as bisulfide complexes and would favor chloride complexes. Thus, we propose that gold precipitation at Nambija occurred by destabilization of chloride complexes due to cooling below 300°C (e.g. Gammons and Williams-Jones, 1997).

A later influx of meteoric fluids leads to the deposition of subordinate comb quartz. Sulfide-rich type III veins were formed during a late pulse of magmatic fluids, which mixed with meteoric fluids. Low-temperature, high-salinity fluids recorded in calcite sealing post-ore normal faults are interpreted to represent basinal brines. The latter probably circulated during the formation of the lower Cretaceous Hollín basin as the normal faults are cut by reverse faults linked to the uplift of the sub-Andean zone that started during the upper Cretaceous.

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