J. Vallance, L. Fontboté, A. Markowski, T. Vennemann, H.J. Stein, U Schaltegger, M. Chiaradia (2006). Hydrothermal fluid evolution and age of the Nambija oxidized gold skarn (Ecuador). Colloque bilan et prospective du GdR TRANSMET. 6-7 July 2006, Nancy, France, p. 162-166.

HYDROTHERMAL FLUID EVOLUTION AND AGE OF THE NAMBIJA OXIDIZED GOLD SKARN (ECUADOR)

J. Vallance [a], L. Fontboté [a], A. Markowski [b], T. Vennemann [c], H.J. Stein [d], U Schaltegger [a], M. Chiaradia [a]

[a] *Section des Sciences de la Terre, University of Geneva, Rue des Maraîchers 13, 1205 Geneva, Switzerland. Jean.Vallance@terre.unige.ch*
[b] *Isotopengeologie und Mineralische Rohstoffe, ETH-Zentrum, C61.1, Sonneggstrasse 5, 8092 Zürich, Switzerland*
[c] *Institut de Minéralogie et Géochimie, Université de Lausanne,L'Humense, CH-1015 Lausanne, Switzerland*
[d] *AIRIE Program, Department of Geosciences, Colorado State University, Fort Collins, CO 80523-1482, USA*

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.

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. (in press).

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.

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 volcaniclastic 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 volcaniclastic rocks of the Piuntza unit, which occurs as a 20-km long, north-trending, contact-metamorphosed lens within the Jurassic Zamora batholith. The skarn is predominantly made up of massive brown garnet (mean Ad_{55}). Subordinate pyroxene-epidote skarn developed mainly at the margins of brown garnet skarn bodies. Mostly idiomorphic garnet (mean Ad_{55}) 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 to red-brown clusters and crosscutting bands (mean Ad_{84}). As is typical for other skarns developed in volcaniclastic rocks, the zoned mineralogy is poorly defined.

Several porphyritic quartz-diorite to granodiorite intrusions crosscut the Zamora granite or the Piuntza unit in the Nambija district. They are present in all studied mines close to the skarn bodies and show pervasive and B vein-controlled K-alteration (K-feldspar> biotite and/or magnetite and/or titanite) grading into endoskarn alteration (Na-rich plagioclase, actinolite, diopside, K-feldspar and/or titanite).

Gold deposition is related to the weak retrograde stage and preferentially occurs in vugs, type I veins (vein nomenclature in Fontboté et al. (2004). Gold was observed in type II veins but not in sulfide-rich type III veins, which crosscut the previous veins. It occurs within milky quartz in vugs and type I veins and was never observed within later comb quartz. Hematite is typically the only opaque mineral in addition to native gold.

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 CO_2 and N_2, with a CO_2 content between 94 and 100 mol%. H_2S was identified in about one third of the inclusions. Carbon dioxide bulk content ranges from 55 to 1.6 mol%, N_2 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 CO_2 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°-74.5°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.

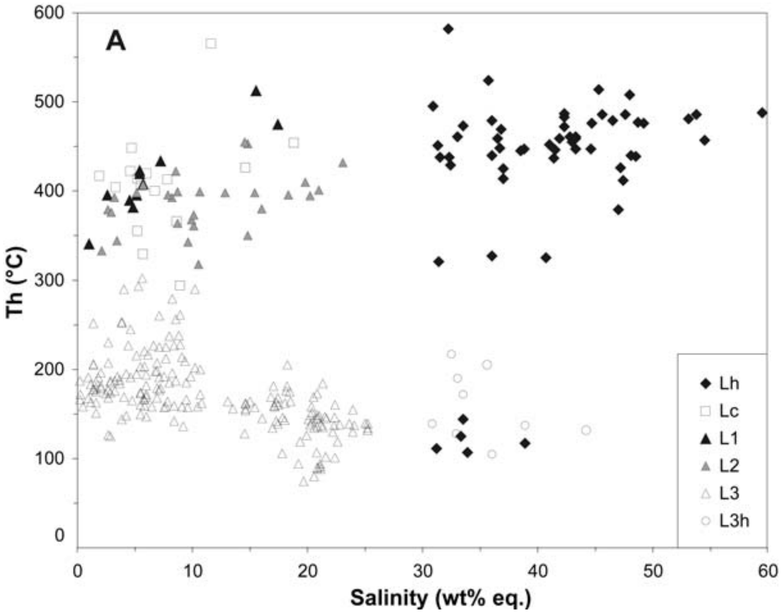

Fig. 1 *Binary plots of temperature of bubble or vapor diseappearrance (Th) vs. Salinity with data ordered by fluid inclusions type*

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 $\delta^{18}O_{water}$ 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 $\delta^{18}O$ values of 7.6 to 6.8‰ and 15 to 14.6‰, respectively. Calcite from vugs and post-ore stage has similar $\delta^{13}C$ values of -8.6 to -10‰ and -8.3 to -8.4‰ respectively, compatible with an igneous source for carbon. The calculated $\delta^{18}O_{water}$ values of calcite from vugs (250°-350°C) and post ore stage (120°-160°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 CO_2-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% CO_2 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 William-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 represents 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.

Acknowledgement

We thank Comcumay S.A., Cominzasa, Compañía Minera del Ecuador – Andos, Compañía Minera sol de Oriente, Cooperativa Once de Julio, and Fortuna Gold Mining Corp. for access to their mines and properties and for their assistance in the field. This investigation was supported by the Swiss National Science Foundation, project n° 2000-062 000.00.

References

Fontboté L, Vallance J, Markowski A, Chiaradia M (2004) Oxidized Gold Skarns in the Nambija District, Ecuador. In: Perrello J, Sillitoe R, Vidal C (eds). Andean Metallogenesis: Soc Econ Geol Spec Pub 11: pp 341-357

Gammons CH, Williams-Jones AE (1997) Chemical mobility of gold in the porphyry-epithermal environment. Econ Geol 92:. 45-59

Hammarstrom JM (1992) Mineralogy and chemistry of gold-associated skarn from Nambija, Zamora Province, Ecuador: A reconnaissance study: Advances related to U.S. and International Mineral Resources, USGS, pp 107-118

Jaillard E, Guillier B, Bonnardot MA, Hassani R, Lapierre H, Toro J (2005) Orogenic buildup of the Ecuadorian Andes. In: Sempéré T (ed). 6th International Symposium on Andean Geodynamics (ISAG 2005, Barcelona), extended abstracts, pp 404-407

Litherland M, Aspden JA, Jemielita RA (1994) The metamorphic belts of Ecuador. Overseas Memoir 11, BGS, Keyworth UK, 147p

Markowski A, Vallance J, Chiaradia M, Fontboté L Mineral Zoning and Gold occurrence in the Fortuna skarn Mine, Nambija district, Ecuador. Mineralium Deposita

Meinert LD (2000) Gold in skarns related to epizonal intrusions. In: Hagemann SG, Brown PE (eds). Gold in 2000, Rev Econ Geol 13, pp 347-375

Pratt WT, Duque P, Miguel P (2005) An autochthonous geological model for the eastern Andes of Ecuador. Tectonophysics 399: 251-278

Prodeminca (2000) Depositos porfidicos y epi-mesotermales relacionados con intrusiones de la Cordillera del Cóndor: Evaluacion de distritos mineros del Ecuador: UCP Prodeminca Proyecto MEM BIRF 36-55 EC 5, 223p