Chapter 19

Oxidized Gold Skarns in the Nambija District, Ecuador

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Abstract

The Nambija gold district, southeastern Ecuador, consists of oxidized skarns developed mainly in volcanoclastic rocks of the Triassic Piuntza unit, which occurs as a 20-km-long, north-trending, contact-metamorphosed lens within the Jurassic Zamora batholith. High gold grades (10–30 g/t) are accompanied in most mines by very low Fe, Cu, Zn, and Pb sulfide contents. The skarn is constituted dominantly by massive brown garnet (mean Ad38). Subordinate pyroxene-epidote skarn developed mainly at the margins of brown garnet skarn bodies. Mostly idiomorphic and more andraditic garnet (mean Ad45) 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 occur largely as honey-yellow to red-brown clusters and cross-cutting bands (mean Ad84). As typical for other skarns developed in volcanoclastic rocks, mineral zoning is poorly defined.

The retrograde overprint is weakly developed, commonly fails to alter the prograde minerals, and is mainly recognized in mineral infilling of structurally controlled (N10°–60°E) vugs and up to several-centimeter-wide type I veins, as well as interstices in blue-green skarn. Retrograde minerals are milky quartz, K-feldspar, calcite, chlorite, and hematite, ±plagioclase, ±muscovite, plus minor amounts of pyrite, chalcopyrite, hematite, sphalerite, and gold. Vugs and type I veins are cut by thin (1–2-mm) throughgoing type II veins that show similar orientations and mineralogy. Native gold is associated with retrograde alteration, mainly in the irregular vugs and type I veins, and subordinately in interstitial spaces and throughgoing type II veins. It is not observed in sulfide-rich type III veins, which cut the previous vein generations.

High-temperature (up to 500°C) and high-salinity (up to 60 wt % NaCl equiv) inclusions in pyroxene represent the best approximation of the fluid responsible for a significant part of the prograde skarn stage. Such a highly saline fluid is interpreted as the result of boiling of a moderately saline (~8–10 wt % NaCl equiv) magmatic fluid at temperatures of ~500°C. Moderate- to low-salinity fluid inclusions (20–2 wt % NaCl equiv) in paragenetically later garnet as well as in epidote and quartz from vugs and type I veins may represent later, slightly lower temperature (~420°–350°C) trapping of similar moderately saline fluids with or without some degree of boiling and mixing. The similarity of salinities and homogenization temperatures in late garnet, epidote, and quartz fluid inclusions is consistent with the apparent continuum between the prograde and retrograde skarn stages, as illustrated by the general lack of prograde mineral alteration, even at the contacts with retrograde fillings.

Gold deposition, together with that of small amounts of hematite, chalcopyrite, and pyrite, took place during fluid cooling in the retrograde skarn stages but not during the last retrograde alteration, as indicated by the absence of gold in the sulfide-rich type III veins. The abundance of gold-bearing samples with high hematite/sulfide ratios and generally low total sulfide contents suggests high oxygen fugacities during gold deposition. The northeast structural control of vugs and type I veins, compatible with regional northeast-striking structures, suggests that skarn formation, including gold deposition in the retrograde stage, took place under conditions of tectonic stress.

Minimum Re-Os ages of 145.92 ± 0.46 and 145.58 ± 0.45 Ma for molybdenite from type III veins are compatible with skarn formation and gold mineralization during Late Jurassic magmatism. A genetic relationship with felsic porphyry intrusions that cut the Jurassic Zamora batholith and crop out near several gold skarns is suggested by a published hornblende K-Ar age of 141 ± 5 Ma for a felsic porphyry in the northern part of the Nambija district. Furthermore, the minimum Re-Os ages of ~146 Ma are just slightly younger than the published K-Ar ages (154 ± 5, 157 ± 5 Ma) for the Pangui porphyry copper belt about 70 km north of Nambija.

Resumen

El distrito aurífero de Nambija, suroeste de Ecuador, está constituido por skarns oxidados desarrollados en rocas volcanoclasticas de la unidad triásica de Piuntza, que ocurre como una lente de 20 km de largo afectada por metamorfismo de contacto dentro del batolito de Zamora.

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Leyes altas de Au (10–30 g/t) son acompañadas en la mayoría de las minas por contenidos bajos en sulfuros de Fe, Cu, Zn y Pb. El skarn está constituido predominantemente por cuerpos masivos de granate marrón (media Ad₁₈). En menor medida se desarrolla un skarn de piroxeno-epidoto en los márgenes de los cuerpos masivos de granate marrón. Granate en general idiomórfico y de composición algo más andradítica (media Ad₃₄) ocurre en un skarn azul-verde formado en una fase más tardía en áreas de alta porosidad situadas en la transición entre skarn masivo y cavidades irregulares y vetas dilacionales de tipo I. Las últimas generaciones de granate son predominantemente andradíticas (media Ad₄₂) y forman predominantemente “clusters” y bandas que cortan los otros tipos de skarn. La zonación mineral no está bien desarrollada, lo que es típico de skarns formados sobre rocas volcánoclasticas.

La fase retrógreda es débil, en general no altera los minerales progradados y se reconoce principalmente en los rellenos de cavidades y vetas de tipo I de hasta algunos cm de espesor que están controladas estructuralmente (N10-60°E), así como en intersticios en el skarn azul-verde. Los principales minerales retrógredos son cuarzo lechoso, feldespatos potásico, calcita, clorita, y hematita, ±plagioclasa, ±muscovita, así como trazas de pirita, calcopirita, hematita, esfalerita y oro. Cavidades y vetillas de tipo I son cortadas por finas (1-2 mm) vetillas de tipo II de similar orientación y mineralogía. El oro nativo está asociado con la alteración retrógreda, principalmente en rellenos de cavidades y venas de tipo I y en menor medida en intersticios y así como en las vetillas cortantes de tipo II. No se observa oro en vetas ricas en sulfuros de tipo III que cortan las generaciones precedentes.

Inclusiones de alta temperatura (hasta 500°C) y alta salinidad (hasta 60% equiv. en peso de NaCl) representan la mejor aproximación al flujo responsable de una parte de la fase prograda. Este flujo muy salino se habría separado por ebullición de un fluido magmáticos de salinidad moderada (8-10% equiv. en peso de NaCl) a temperaturas de ~500°C. Inclusiones fluidas de salinidad moderada a baja (20-2% equiv. en peso de NaCl) en granate paragenéticamente tardío y en epidoto y cuarzo de vetas de tipo I, pueden representar el entramamiento de fluidos similares de salinidad moderada que pueden haber sido afectados en alguna medida por ebullición y mezcla con otros fluidos. La similitud de salinidades y temperaturas de homogenización de inclusiones fluidas en granate tardio, epidoto y cuarzo es compatible con la continuidad apparente entre las fases pro- y retrógreda, que es ilustrada por la poca alteración de los minerales progradados, incluso en contacto con rellenos de minerales retrógredos.

La precipitación de oro, junto a la de pequeñas cantidades de hematita, calcopirita, y pirita, tuvo lugar durante el enfriamiento en la fase retrógreda, pero no en las últimas etapas de ésta, como indica la ausencia de oro en las vetas III ricas en sulfuros. La abundancia de muestras con oro que presentan razones altas de hematita/sulfuros y el contenido en general muy bajo en sulfuros sugieren altas fugacidades de oxígeno durante la precipitación del oro. El control estructural de cavidades y vetas de tipo I, compatible con estructuras regionales de rumbo noreste, y que en parte tienen un carácter dilacional, sugiere que la formación del skarn, incluyendo el depósito de oro en la fase retrógreda, tuvo lugar bajo condiciones de esfuerzo tectónico.

Edades mínimas de Re-Os de 145.92 ± 0.46 y 145.58 ± 0.45 Ma en molibdenitas de vetas de tipo III son compatibles con la formación del skarn y la mineralización de oro durante el magmatismo del Jurásico tardío. Una edad publicada de 141 ± 5 Ma (K-Ar en hornblenda) en un pórfiro felsico en el norte del distrito de Nambija apoyaría una relación genética con las intrusiones porfíricas felsicas que cortan el batolito jurásico del Jurásico tardío. La precipitación de oro, junto a la de pequeñas cantidades de hematita, calcopirita, y pirita, tuvo lugar durante el enfriamiento en la fase retrógreda, pero no en las últimas etapas de ésta, como indica la ausencia de oro en las vetas III ricas en sulfuros. La abundancia de muestras con oro que presentan razones altas de hematita/sulfuros y el contenido en general muy bajo en sulfuros sugieren altas fugacidades de oxígeno durante la precipitación del oro. El control estructural de cavidades y vetas de tipo I, compatible con estructuras regionales de rumbo noreste, y que en parte tienen un carácter dilacional, sugiere que la formación del skarn, incluyendo el depósito de oro en la fase retrógreda, tuvo lugar bajo condiciones de esfuerzo tectónico.

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In a reconnaissance study, Hammarstrom (1992) interpreted the Nambija district as a “gold-associated skarn.” Nambija is described by Meinert (1998) as an “oxidized gold skarn” in a worldwide compilation of gold-bearing skarns. The most comprehensive investigation of the geology and ore deposits of the Nambija district was carried out by the British
Geological Survey (Litherland et al., 1994; Prodeminca, 2000), who proposed that the gold mineralization overprints skarn bodies “under epithermal conditions.” Herein, we present evidence supporting a skarn-related origin for the Namibia gold mineralization.

This paper summarizes the preliminary results of an ongoing study (Markowski, 2003; Vallance et al., 2003). The study does not include comprehensive geologic mapping of the Namibia district, a necessary but not easy undertaking because of the poor outcrop conditions prevailing in a region covered by tropical vegetation. Our study is based on partial mapping of the Fortuna, Guaysimi, and Campanillas mines and selected observations in the Namibia (El Tierrero, Playón, and Mapasingue) and Cambana mines. A total of 278 thin and polished sections were studied, and microprobe (40 samples), XRF (30 samples), and microthermometric analyses (25 samples) were performed. Analytical conditions are detailed in the tables or figures in which the results are presented. More detailed studies on the Fortuna mine and on fluid inclusions from the entire district are in preparation (Markowski et al., in prep; Vallance et al., in prep).

**Geologic Setting**

Central and western Ecuador consists of a complex mosaic of terranes (Fig. 1), each a few tens of kilometers wide and
The strike and dip of the Piuntza unit are visible because of the intercalations of black silty shale and black silty sandstone. Black silty sandstone, black silty shale, and coarse-grained tuff, volcanic flows, and volcaniclastic breccia as well as limestone and calcareous shale. At sites studied during this work, the Piuntza unit consists mainly of volcaniclastic rocks of basaltic andesite to andesite composition (Markowski, 2003) and quartzite. Two- to 20-cm-thick levels of black silty shale are commonly intercalated with volcaniclastic rocks and quartzite; limestone is only a minor component. The volcaniclastic rocks in places show erosion channels, matrix-supported sedimentary breccia horizons, and synsedimentary tilted blocks. All these features suggest a dominantly continental depositional environment. Litherland et al. (1994) mentioned an increase of the volcanic component to the north of the Nambija district and of marble to the south. 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garnet skarn). In the latter deposit, bivalve relicts occur in green pyroxene skarn, and at Fortuna bioclasts occur in unskarnified volcaniclastic rocks (Markowski, 2003).

At the outcrop scale, the skarn forms mainly concordant bands a few tens of centimeters to a few meters thick (in Guaysimi-Central up to 10 m; Fig. 4), whose morphology is largely controlled by bedding and unreactive and/or less permeable lithologies like sandstone, black silty shale, and massive volcanic horizons. The transition from skarn to volcaniclastic rocks is usually sharp. The skarn bodies show typical features of metasomatic replacement including irregular limits giving rise to a spotted aspect (Fig. 5a).

The main skarn type is brown garnet skarn consisting of massive coarse-grained garnet ± pyroxene (Figs. 3–5a, b, e). Garnet is anhedral to subhedral (Fig. 5e) and has mainly granitic compositions (mean Ad$_{35}$ range Ad$_{51-20}$ Fig. 6; Table 1). It has a dirty appearance, because it replaced volcaniclastic rocks, and contains numerous dark rutile needles. Only locally are garnet cores altered to chlorite, calcite ± hematite during retrograde alteration, with garnet rims remaining unaltered.

A second skarn type, green pyroxene-epidote skarn, consists of pyroxene, epidote ± garnet, and K-feldspar. Pyroxene is mostly diopsidic (Di$_{92-47}$), with Mn contents that may be significant (Jo$_{0-19}$). Epidote is locally abundant and, at Fortuna, has Ep$_{10-18}$ compositions (Markowski, 2003). Green pyroxene-epidote skarn occurs generally at the margins of brown garnet skarn bodies as centimetric to decimetric rims (Figs. 3b, 4b). At Guaysimi-Central and mainly Fortuna mine 1 (Markowski et al., in prep), green skarn forms relatively thick bodies mappable at the deposit scale and, at least at Fortuna, are distal relative to the main skarnified area (mine 2). Locally, pyroxene is partly altered to chlorite, calcite ± hematite during retrograde alteration (Fig. 3b).

The proportion of brown skarn bodies displaying a green skarn margin versus direct transition to unskarnified rocks varies from <10 percent at Guaysimi-Central to 50 percent at Campanillas. The contact from green skarn to unskarnified volcaniclastic rocks is commonly marked by a discontinuous, 0.5- to 2-cm-thick rim of K-feldspar, locally also observed at the contacts of brown garnet skarn (Fig. 4b, insets a and d).

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**FIG. 3.** a. Lithologic column for the Campanillas main open pit, showing the three main skarn bodies. The skarn morphology is controlled by lithology; bedding is revealed by the unskarnified black shale horizons. The black outline shows the location of the map presented in (b). b. Bench map of a typical site including all observed skarn types plus metamorphosed volcaniclastic rocks and black shale intercalations. Green pyroxene-epidote skarn is more affected by retrograde alteration than brown garnet skarn. Bench location is indicated in Figure 8.
Fig. 4. a. Lithologic column for the Guayzimi-Central mine (9546, 150N, 747,630E). Inset: Location of the detailed bench description shown in (b). b. Bench map, showing relationships between volcaniclastic rocks, skarn types, vugs, and veins. Insets: a. Transition from brown skarn to blue-green skarn and vugs. Volcaniclastic rocks, brown skarn, and blue-green skarn are cut by honey-yellow garnet bands. b. Type I veins crosscut by type II veins. c. Gold-bearing (Au) vug filled with K-feldspar (kfs), plagioclase (pl), and quartz (qtz) and crosscut by type II veins. d. Green skarn between massive brown skarn and volcaniclastic relict; at the contact with the latter there is a discontinuous band of K-feldspar. A honey-yellow garnet band cuts everything.
A striking characteristic of the Nambija skarns is the widespread presence of vugs, some elongate, which often grade into 2- to 30-cm-thick discontinuous type I veins aligned in preferential directions (Figs. 5b-d, 7). Vugs and type I veins are filled, in order of decreasing abundance, by anhedral milky quartz, K-feldspar, ±calcite, ±chlorite, ± epidote, ± plagioclase ± muscovite and, in places, by subordinate pyrite, hematite, sphalerite, chalcopyrite, and native gold (Figs. 5h-j), all minerals considered to have precipitated during the retrograde stage (Fig. 8). Vugs and type I veins show gradational contacts with the massive skarn (Fig. 5b), with infill minerals typically cementing euhedral garnet at the vug and/or vein walls (Fig. 5g). This late garnet does not show corrosion against the retrograde minerals. In places, small geodes with clear colorless to purple, subhedral quartz are observed in the center of the veins. In several mines, including Guaysimi, Nambija, Campanillas, and Cambana, the vugs and veins are aligned preferentially along N10° to N60°E directions and have steep dips (Fig. 9a). These orientations are consistent with the northeast-southwest structural control of the gold mineralization reported by Prodeminca (2000) and may represent dilational openings. Alternatively, in places, they are roughly concordant to bedding (Fig. 4b, inset b).

Type I veins also cut volcaniclastic rocks up to a few tens of meters from the skarn front (Fig. 9b), where they have sharper contacts and are narrower than where they cut skarn. The spacing between type I veins ranges from a few to tens of meters (Fig. 9a), and no evidence of vertical movement is observed.

A transition zone of blue-green garnet skarn commonly occurs between brown garnet skarn and vugs and type I veins. It consists of dominantly euhedral garnet, with minor amounts of pyroxene and epidote, cemented by large anhedral grains of quartz and K-feldspar (Figs. 4b, 5b). Garnet is more transparent and shows more andraditic compositions (mean Ad45, range Ad99–20; Fig. 6; Table 1) than that in the massive brown skarn. Some garnet cores are affected by retrograde alteration. Quartz may constitute up to 50 percent and even more of this transition zone. The milky quartz and K-feldspar filling the pores of the blue-green garnet skarn are assigned to the retrograde stage, as also suggested by the transitional position between vugs and/or type I veins and the massive brown garnet skarn. The fact that garnet alteration, typically into chlorite, calcite, ± hematite (Fig. 5f), is more frequent in the blue-green garnet skarn (though still weak and only affecting the cores) supports this interpretation.

The most andraditic compositions are found in honey-yellow to red-brown garnet (mean Ad84, range Ad100–46; Fig. 6; Table 1) that occurs mainly as millimeter-thick, irregular bands (Fig. 5c), which cut all skarn types and volcaniclastic rocks and which, in part, rim vugs and veins typically filled with calcite, chlorite, and quartz (without K-feldspar and gold). Garnet displays strong oscillatory zoning (Fig. 5g), with almost pure andraditic compositions being more abundant toward the rims. Honey-yellow to red-brown garnet also occurs as clusters within the brown garnet skarn giving it a mottled appearance (e.g., right part of Fig. 5b). The clusters are up to 10 mm in diameter but generally smaller.

The different skarn facies and the fillings of vugs and type I veins are frequently crosscut by thin (<1-mm) type II veins displaying sharp contacts (Figs. 5d, 7). They occur mostly as bundles (Figs. 4b, 5d, 9b) and roughly follow the same orientations (N10°–60°E) and dips of type I veins. The infill mineralogy is similar to that of type I veins but with calcite...
present and sulphides slightly more abundant (but still <5%). A key difference from type I veins is their throughgoing character. Type II veins are observed in all deposits studied except Fortuna. A later vein generation comprises steeply dipping N70°- to 100°E-trending type III veins, which cut vugs and types I and II veins (Fig. 7). They are much richer in sulphides, typically granular pyrite (5–50 vol%), and in places they contain sphalerite and molybdenite. Other infill minerals are similar to those in type II veins. Their thickness ranges from 1 to 2 mm but can reach a few centimeters. At Guaysimi-Central, type III veins cutting volcaniclastic rocks show an alteration halo of chlorite and calcite ± epidote.

At Guaysimi-Banderas (Fig. 2), steep 1- to 2-mm (up to 1-cm)-wide type III veins cut volcaniclastic rocks, are filled by quartz and granular pyrite, and display quartz-sericite halos similar to the D veins defined by Gustafson and Hunt (1975) in the porphyry copper environment. Such quartz-sericite alteration is not recognized in the skarn.

Sealing of N10°- to 70°E-striking late normal faults (vertical movement of centimeters to meters) by calcite ± quartz (Fig. 5b) constitutes the last vein generation. At Guaysimi-Central, these calcite veins are cut by east- to southeast-trending reverse faults dipping at 10° to 40° south.

Mineralization and Ore Geochemistry

Native gold, in grains up to several millimeters in size, together with retrograde quartz, K-feldspar, garnet, and calcite, occurs preferentially in vugs (Fig. 5b) but mainly in type I veins in skarn bodies (Figs. 4b inset c, 5h-j, 9b). Subordinately, gold occurs in type II veins but is not observed in type III veins. 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. Retrograde alteration is generally weak and, in places, is expressed only by quartz, K-feldspar, and calcite filling interstitial spaces between unaltered garnet and pyroxene grains (Fig. 5j). Thus, cursory observation could lead to the erroneous conclusion that gold occurs in unaltered skarn.

Type I veins are also gold bearing where crosscutting volcaniclastic rocks but, like the type I veins themselves, always within a few tens of meters distance from the skarn front. At Sultana del Cóndor (Fig. 2), gold is reported to occur in fractures up to a few meters from the skarn bodies, always “associated to K-feldspar alteration” (Prodeminca, 2000, p. 109; A. Eguiz, pers. commun., 2003). Gold contains 1 to 15 wt percent Ag and <1 wt percent Hg (Litherland et al., 1994; Paladines and Rosero, 1996; Prodeminca, 2000; Markovski, 2003).

Hematite is a subordinate mineral at Nambija but is relatively common in vugs and type I veins, typically as the only opaque mineral in addition to native gold (Fig. 5h). In contrast, although some pyrite, chalcopyrite, and sphalerite are found together with gold, the presence of native gold does not correlate with total sulphides. The native gold is often observed in vugs and type I veins devoid of sulphide minerals, and the sulphide-rich type III veins are barren.

The total amount of sulphide minerals (pyrite > chalcopyrite > sphalerite) is remarkably low in the Nambija deposits, typically <1 percent, and in numerous mineralized samples visible sulphide minerals are absent. As noted above, the content of sulphide minerals increases progressively from type I to type III veins.

Sphalerite abundance is variable; traces are found in vugs and type I veins at Campanillas and Guaysimi; larger amounts occur as disseminated grains forming centimeter-thick bands along the inner side of the skarn front against limestone at Nambija-El Diamante, where grades of >5 percent Zn are reported (Cooperativa 11 de Julio and Gribipe, 2000). Similar sphalerite disseminations are also observed in volcaniclastic rocks a few centimeters from the skarn front at Campanillas.

Major and trace element analyses were performed on 50 selected mineralized samples (300–1,000 g each) by XRF and neutron activation and on some gold-rich samples by fire assay with gravimetric finish. Bismuth and Te were analyzed by atomic absorption. The results are presented in Figure 10 and Table 2, which includes the analytical details. Because of the limited size of the analyzed samples, the results are only indicative and true metal contents cannot be inferred from them.

The highest gold contents were observed in samples from vugs and type I veins at Guaysimi (up to 1,020 ppm) and Campanillas. The low total sulphide contents are reflected by chemical analyses. All but two samples have <1 and most <0.1 wt percent S. In support of the petrographic observations, gold does not correlate with Cu, Zn, S, and As (Fig. 10). As shown in Figure 10c, gold-rich samples (Au >100 ppb) frequently possess S, Cu, and Zn contents of <100 ppm. Some samples show even higher Au than Cu and Zn contents (e.g., sample DTR 105, Table 2).

**FIG. 5.** Typical skarn and gold mineralization in the Nambija district. a. Spots of brown skarn (bsk) in volcaniclastic rocks (vr) in the Guaysimi-Central mine. b. Transition from brown skarn to blue-green skarn (bgsk) and vugs. Honey-yellow garnet clusters (hgt) occur in the brown and blue-green skarn. The vug on the left is filled with late garnet (grt), K-feldspar (kfs), quartz (qtz), hematite (hm), and chlorite (chl). Native gold grains (Au) occur preferentially at the contact between garnet and quartz (Campanillas main present open pit, sample DTR 380). c. Honey-yellow garnet bands in brown garnet skarn. In part they form a rim around vugs filled by calcite and chlorite. (Campanillas main present open pit, sample DTR 327). d. Type II veins crosscutting brown skarn, blue-green skarn, and vugs at Guaysimi-Central mine. Vugs and type II veins contain gold (sample DTR 305). e. Anhedral to subhedral anisotropic garnet in brown garnet skarn (Campanillas main present open pit, sample DTR 380, transmitted light). f. Idiomorphic garnet cemented by milky quartz in blue-green garnet skarn. Garnet cores have calcite (cal) inclusions, product of weak retrograde alteration (Campanillas main present open pit, sample DTR 380, transmitted light). g. Honey-yellow garnet band in brown garnet skarn, showing zoning from grandite (anisotropic bands) to pure andradite (isotropic rim). The vein grades laterally into a vug filled by calcite (Campanillas main present open pit, sample DTR 327). h. Outcrop of gold-bearing type I vein in the Campanillas main present open pit. The vein is filled with quartz, hematite, and chlorite. i. Gold between garnet, quartz, and calcite in type I vein at the Guaysimi-Central mine. The garnet core shows retrograde alteration to calcite and chlorite (sample DTR 305, transmitted light). j. Gold together with late garnet, quartz, and K-feldspar in a type I vein at the Guaysimi-Central mine (sample DTR 305, reflected light).
Antimony and As contents are also very low (Sb <10 ppm, As <120 ppm; Fig. 10e). Antimony is more abundant in the green pyroxene-epidote skarn and As in the brown garnet and blue-green garnet skarn. At Fortuna, green pyroxene skarn is interpreted to occupy a distal position with respect to the main skarn area (Markowski et al., in prep). Although Litherland et al. (1994, p. 93) documented the presence of Bi tellurides intergrown with gold at Campanillas, the contents of Bi and Te are also extremely low (<10 ppm) in the analyzed samples.

Fluid Inclusions

The first stages of an ongoing fluid inclusion study investigated prograde garnet and pyroxene, retrograde epidote, and quartz in vugs and type I veins, as well as calcite (sealing normal faults) from Fortuna (n = 63), Cambana (n = 34), Campanillas (n = 44), Nambija (n = 19), and Guaysimi (n = 62). Late blue-green skarn garnet and honey-yellow garnet contain suitable inclusions, but the early and volumetrically dominant brown skarn garnet is too dirty and opaque for meaningful fluid inclusion study. Heating and freezing analyses were obtained on ~100-µm-thick, doubly polished rock sections with a Linkam stage, as described by Shepherd (1981).

The results are similar for all studied deposits. Five fluid inclusion types are distinguished (Fig. 11). Inclusions containing at least one solid phase are termed Lh. Two-phase fluid inclusions (L) show a decrease of the V/L ratio as their homogenization temperatures decrease (L1–L3). Vapor-rich fluid inclusions show V/L ratios between 0.9 and 1. All fluid inclusions show eutectic temperatures below –40°C, indicating the presence of cations like Ca²⁺, Mg²⁺, or Fe²⁺/Fe³⁺.

The salinity vs. T_h plot (Fig. 11) shows a group of high-temperature inclusions (mainly ~400°C–500°C) occurring both in prograde pyroxene and garnet and retrograde quartz and epidote. Another group occurs as secondary L3 and Lh lower temperature inclusions (<300°C) in quartz.

The pyroxene fluid inclusions (Lh) record the highest homogenization temperatures (mainly 500°C–430°C) and salinities (12–60 wt % NaCl equiv). Inclusions in garnet (L1-2) are of slightly lower temperature (mainly 450°C–390°C) and salinity (20.2–2.6 wt % NaCl equiv), with those in garnet from blue-green skarn displaying higher temperatures and

![Diagram](image-url)
VUGS AND VEINS IN THE NAMBIJA DISTRICT

<table>
<thead>
<tr>
<th>Key features</th>
<th>Observations</th>
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<tbody>
<tr>
<td>Diameter ranges from several millimeters to 15 cm. Rarely occur in volcaniclastic rocks. Quartz-K-feldspar ratio variable. Vugs occur in all mines of the Nambija district. See also Figs. 3a, c and 4b, f.</td>
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<tr>
<td>Type I veins</td>
<td>Widths range from 2 to 30 cm. Walls are better defined than in vugs particularly where cutting volcaniclastic rocks. Quartz-K-feldspar ratio is always &gt;1:1. Highest gold grades. Typically well developed at Campanillas and to a lesser extent at Guaysimi, recognized at Cambana, but virtually absent at Fortuna. See also Figs. 3b, 4c, d, e, 7a, b.</td>
</tr>
<tr>
<td>Type I veins (N10-60°E)</td>
<td>They are thin (&lt;1 mm) and occur mostly as bundles of parallel veins. Sulfide content &lt;5%. Typically well developed in the Guaysimi Central mine. Occur sometimes at Campanillas and in El Tierreo mine. Always cut type I veins. See also Figs. 3b, c, 4f, and 7b.</td>
</tr>
<tr>
<td>Type II veins (N10-60°E)</td>
<td>Thickness is mainly in the range of 1 to 2 mm but up to a few cm. Sulfide content 5 to 50% (sphalerite and molybdenite observed). Well developed in the Katy area at Campanillas, in El Tierreo mine at Nambija, and at Guaysimi. Actinolite observed at Guaysimi Central.</td>
</tr>
<tr>
<td>Type III veins (N70-100°E)</td>
<td>Thickness is mainly in the range of 1 to 2 mm but up to a few cm. Sulfide content 5 to 50% (sphalerite and molybdenite observed). Well developed in the Katy area at Campanillas, in El Tierreo mine at Nambija, and at Guaysimi. Actinolite observed at Guaysimi Central.</td>
</tr>
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</table>

Fig. 7. Main features of structurally controlled vugs and vein types in the Nambija district. Vugs and type I veins are interpreted as dilational features. Abbreviations: Au = gold, grt = garnet, kfs = K-feldspar, qtz = quartz, py = pyrite. See Figure 9b for typical internal structure of type I veins.
salinities than those in late garnet (Fig. 11). As mentioned above, no suitable inclusions in the dominant but dirty brown garnet skarn were found. Similar temperatures, salinities, and V/L ratios (L1–L2) are observed in fluid inclusions in epidote as well as in those occurring as clusters in milky quartz (422°–345°C, 10.6–1.9 wt % NaCl equiv).

Homogenization temperatures of <300°C, mainly between 250° and 150°C, are observed in secondary L3 inclusions in milky quartz which display a wide salinity range (0.1–25 wt % NaCl equiv), with values clustered around 2 to 8 and 15 to 22 wt percent NaCl equiv. In the same temperature range, high-salinity Lh inclusions (31–44 wt % NaCl equiv) occur, in places, in clear pyramidal quartz of type I veins (Campanillas) and as secondary inclusions in milky quartz (Fortuna). The fluid inclusions in the calcite sealing in normal faults record low-temperature (94°–75°C) intermediate-salinity fluids (21.3–23.1 wt % NaCl equiv). Similar moderate to low temperatures and salinities were found in quartz and calcite by T. J. Shepherd (1988, in Litherland et al., 1994).

Re-Os Molybdenite Ages in Type III Veins

In the El Tiertero mine at Nambija, 2- to 5-cm-wide, skarn-hosted type III veins contain quartz, K-feldspar, epidote, calcite, pyrite, chalcopyrite, molybdenite, and/or sphalerite and cut vugs and type I veins. Two molybdenite samples from the type III veins were separated at AIRIE in Colorado and yielded Re-Os ages of 145.92 ± 0.46 and 145.58 ± 0.45.
Ma (H. Stein, AIRIE Colorado, in Vallance et al., in prep.). It should be pointed out that the dated molybdenite was not taken from molybdenite-bearing quartz-rich and sulfide-poor A or B veins crosscutting the El Tierro porphyry (Prodem-inca, 2000, p. 87) but in sulfide-rich type III veins crosscutting the skarn, which can be compared to D veins in a porphyry systems (see above).

Discussion and Conclusions

Skarn evolution

As in other skarns developed in volcaniclastic rocks (Newberry et al., 1997; L. Meinert, pers. commun., 2004), mineral zoning is not well defined in the Nambija district. The bedding-parallel form of most skarn bodies is explained by

![Log-log plots of trace element analyses for selected mineralized samples from the Nambija district (see Table 2). No correlation is observable between (a) Au and Cu, (b) Au and Zn, (c) Au and S, and (d) Au and As. A positive correlation is observable between (e) S and Zn + Cu in vugs and type I veins. (f). Sb vs. As indicates a preferential spatial association of antimony with green skarn and arsenic with brown skarn ± blue-green skarn.](image_url)
differences in permeability and reactivity of the Triassic Pi-
utza unit. The dominance of garnet over pyroxene is char-
acteristic of oxidized gold skarns (Meinert, 1998). The ob-
served evolution from granitic to andraditic compositions
with time, a common feature in many skarns, may be due to
progressively more oxidizing conditions, lower temperatures
of formation, and/or salinity decreases (Einaudi et al., 1981;
Jamtveit et al., 1995; Newberry et al., 1997).

A salient feature of the Nambija skarn is the poor imprint
of the retrograde stage, which does not affect most of
the massive brown garnet skarn, is only slightly better expressed
in the green pyroxene-epidote skarn, and is mainly developed
as infill of structurally controlled (N10°–60°E) vugs and veins
and in an intergranular position in the transitional blue-green
garnet skarn. The mineral association of the retrograde skarn,
milky quartz, K-feldspar, calcite, chlorite, hematite, and/or
pyrite is typical for oxidized gold skarn deposits (e.g., Red
Dome, Australia, and Mc Coy, Nevada; Ewers and Sun, 1989;
Brooks et al., 1991; Meinert, 1998). The general absence of
corrosion of garnet borders, including those on vug and type
I vein walls, suggests a continuous process encompassing both
the prograde and retrograde stages.

Fluid

Given the impossibility of obtaining fluid inclusion data
from the brown skarn garnet, the high-temperature (up to
580°C), high-salinity (up to 60 wt % NaC equiv) fluid inclu-
sions in pyroxene represent the best approximation to the
fluid conditions during a significant part of the main prograde
stage. Such a highly saline fluid could have been segregated
directly from a magma at 200 MPa (Cline and Bodnar, 1991)
or, alternatively, it may be interpreted as the result of boiling
of a moderately saline (~8–10 wt % NaCl equiv) magmatic
fluid (Burnham, 1979) at temperatures of ~500°C. We prefer
the second explanation because there is no trace of high-salin-
ity fluid in the paragenetically later garnet. The moderately
saline fluid may correspond to contraction of a vapor sepa-
rated at depth from magmatic fluid, as proposed by Heinrich
(2003) for some porphyry copper systems or, alternatively, to
the magmatic fluid itself, which would not have undergone
boiling because it did not intersect the solvus along the cool-
ing path, as suggested by Meinert et al. (1997) for the Big
Gossan skarn deposit.

The moderate- to low-salinity L1 and L2 fluid inclusions
(20–2 wt % NaCl equiv) in paragenetically later garnet as well
as in epidote and quartz from vugs and type I veins may rep-
resent trapping, at a later stage and slightly lower tempera-
ture (420°–350°C), of similar moderately saline fluids with or
without some degree of boiling and mixing. The similarity in
salinities and homogenization temperatures between L1 and
L2 fluid inclusions in late garnet, epidote, and quartz is con-
sistent with the apparent continuum between the prograde
and retrograde stages suggested by petrographic observations.

The wide salinity range in secondary liquid-rich L3 and Lh
fluid inclusions in quartz, with homogenization temperatures
of ~200°C, may point to mixing of saline to moderately saline
fluid with meteoric water, perhaps combined with posttrap-
ping modification leading to salinity increase (Audétat and
Günther, 1999). A boiling hypothesis is unlikely, as it would
require unrealistically low pressures. We do not have good
time constraints for these secondary quartz fluid inclusions: they may have formed much later and by different processes than the skarn mineralization. The presence in the late calcite sealing normal faults of low-temperature (94°–75°C) fluid inclusions with salinities of ~21 to 23 wt percent NaCl equiv suggests ingress of sedimentary brine. Such brine could also have contributed to the secondary fluid inclusions in quartz.

**Paragenetic position of gold and its precipitation**

Gold is spatially associated with the retrograde alteration. This is observed at both orebody and outcrop scales, as only areas affected by retrograde alteration are mineralized, as well as both at sample and microscopic scales, with gold infillings of vugs and N10°E- to N60°E-trending types I and II veins in the same paragenetic position as retrograde milky quartz, K-feldspar, chlorite, and calcite.

These observations imply gold precipitation during the retrograde stage but not during the latest retrograde alteration, as indicated by an absence of gold in the sulfide-rich type III veins. At temperatures of 300° ± 50°C, gold can be transported as hydrosulfide or chloride complexes (Benning and Seward, 1996; Gammons and William-Jones, 1997; Gibert et al., 1998). The frequent association of gold-mineralized samples with high hematite/pyrite ratios and the general low
sulfide and metal contents suggest high oxygen fugacity during gold deposition. The low sulfur and metal contents of mineralized samples from the Nambija skarns (S, Cu, Zn, and As contents typically <100 ppm; Sb, Bi, and Te <10 ppm) are comparable to those reported for the McCoy oxidized gold skarn (Meinert et al., 1990) but, for most elements, lower by a factor of 10 or more than those in the reduced gold skarns of Buckhorn Mountain, Washington (Hickey, 1992), Fortitude, Nevada (Meinert et al., 1990), Ortosa, Spain (Fuertes-Fuente et al., 2000), and some Alaskan deposits (Newberry et al., 1997). The oxidizing character of the fluid would favor gold transport as chloride complexes and precipitation by cooling. In contrast, the bonanza grades encountered at several places at Nambija and the lack of correlation between gold and base metals are difficult to explain simply in terms of cooling and point rather to rapid destabilization of gold-bearing complexes. However, there are no indications of precipitation by destabilization of hydrosulfide complexes, as gold deposition is not accompanied by oxidation nor by a distinct sulfide phase that could have destabilized the complex.

Age and relationship to magmatic activity and tectonics

The Re-Os ages (145.92 ± 0.46 and 145.58 ± 0.45 Ma) obtained on molybdenite from sulfide-rich type III veins at Nambija-El Tierrero are minimum ages for the gold mineralization, as the sampled type III veins cut vugs and type I veins and elsewhere in the district, type III veins also cut type II veins. These ages coincide within error with the 141 ± 5 Ma K-Ar hornblende age reported by Prodeminca (2000) for the quartz monzonite porphyry intrusion at the Cumay-Cu-Mo prospect (Fig. 2) and are slightly younger than K-Ar ages of 154 ± 5 Ma (whole rock) and 157 ± 5 Ma (hornblende) obtained at San Carlos and Panantza, 70 km to the north of the Nambija district, from felsic porphyry intrusions from the Late Jurassic Pangui porphyry copper belt (Fig 1; Gendall et al., 2000; Prodeminca, 2000). Like the Nambija district, the porphyry intrusions of the Pangui belt crosscut the Zamora batholith. Much younger K-Ar ages on vein (Cumay) and alteration minerals (El Tierrero) obtained by Prodeminca (2000) may be the result of disturbance.

The similar mineralogic compositions and evolution of geometric characteristics may suggest that type III veins were formed during the last stages of the retrograde event as part of the same cooling process during which veins developed increasingly sharp boundaries, sulfide contents augmented, and wall-rock alteration became more important. If this assumption is correct, the molybdenite Re-Os ages of ~146 Ma would be not only minimum ages but also closely date the gold mineralization, which, according to the imprecise K-Ar age, would be coeval with the Cumay porphyry intrusion. Therefore it is tentatively proposed that the Nambija gold skarn is related to Late Jurassic porphyry intrusions that cut the Mid-Jurassic Zamora batholith. However, it is also possible that a time gap exists between types I and II and type III veins, which could also explain their different orientations (N10°–60°E and N70°–100°E, respectively). Additional age determinations and mapping of crosscutting relationships between skarns, felsic porphyry intrusions, and alteration attributed to them are necessary to clarify this point and also determine if the porphyry intrusions belong to late phases of the Zamora batholith or constitute an independent magmatic event.

Lead isotope compositions of sulfide minerals from the Nambija skarns (Chiaradia et al., 2004) partly overlap those of the Jurassic Zamora batholiths and porphyries from the Nambija district, supporting derivation of at least part of the lead in the Nambija mineralization from Jurassic magnas.

The results reported herein do not support the genetic interpretation of Prodeminca (2000) for the origin of the Nambija gold deposits. According to Prodeminca (2000, p. 182), the Piuntza unit was metamorphosed by contact with the Zamora batholith during the Jurassic, with local development of clinopyroxene skarn. Extensive granite skarn would only have developed concomitantly with emplacement of mid-Cretaceous porphyry copper stocks. Based mainly on K-Ar dates for K-feldspar, it is further claimed that gold precipitated under epithermal conditions (p. 89) during the Late Cretaceous and/or Paleocene in northeast-trending faults and veins, in part as the result of remobilization of skarn components.

Our results confirm the northeasterly structural control, the main direction of the gold-bearing vugs, and types I and II veins. However, this structural direction was not a late addition but already existed at the end of the prograde stage, as a control of the dilational fillings represented by the vugs and type I veins, and was perpetuated during the retrograde stage as shown by the development of the throughgoing type II veins. In other words, skarn development, including gold deposition during the retrograde stage, took place during conditions of tectonic stress. The N10° to 60°E orientations of vugs and type I and II veins are also compatible with the regional northeasterly structures (Fig. 2), in part described as tensile fractures (Prodeminca, 2000), and with a stress field controlled by northeast-directed subduction as prevailed during the Late Jurassic (Litherland et al., 1994). This scenario accords with the minimum Re-Os age of ~146 Ma for skarn and gold mineralization.

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