

Huanuni, Bonanza and La Suerte Mines: Mineralogy, Geochemistry and Structure

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Abstract. The polymetallic mineralization veins of the world class Huanuni district in Bolivia form a conspicuously intricate framework. Comprehensive study on the mineralogy of proximal and distal deposits indicates that In is preferably concentrated in sphalerite precipitated in a lower-temperature stage in the distal domain. Other strategic elements reported to concentrate in equivalent deposits (e.g. Ga, Ge, Nb, Ta), though, returned very low or no detectable concentrations. Mineral paragenesis and textures and sulfur isotopic data support a complex mineralization history that probably implied multi-episodic intrusive events.

Keywords. Vein, Indium, Tin porphyry, S isotopes

1 Introduction

Operated by the state corporation COMIBOL (Corporación Minera de Bolivia; www.comibol.gob.bo/huanuni), and with an estimated production of 3.000 tons per day in 2014, the world class Huanuni Sn-W-Pb-Ag-Zn deposit is the first tin producer in Bolivia and, along with San Rafael in Peru, worldwide. Scarce works reporting its general features include those by Schneider-Scherbina (1964), Arce (2009) and Arqués et al. (2012).

Bolivian Sn-W deposits are reported to present potential as hosts of strategic metals such as In, Ga, Ge,

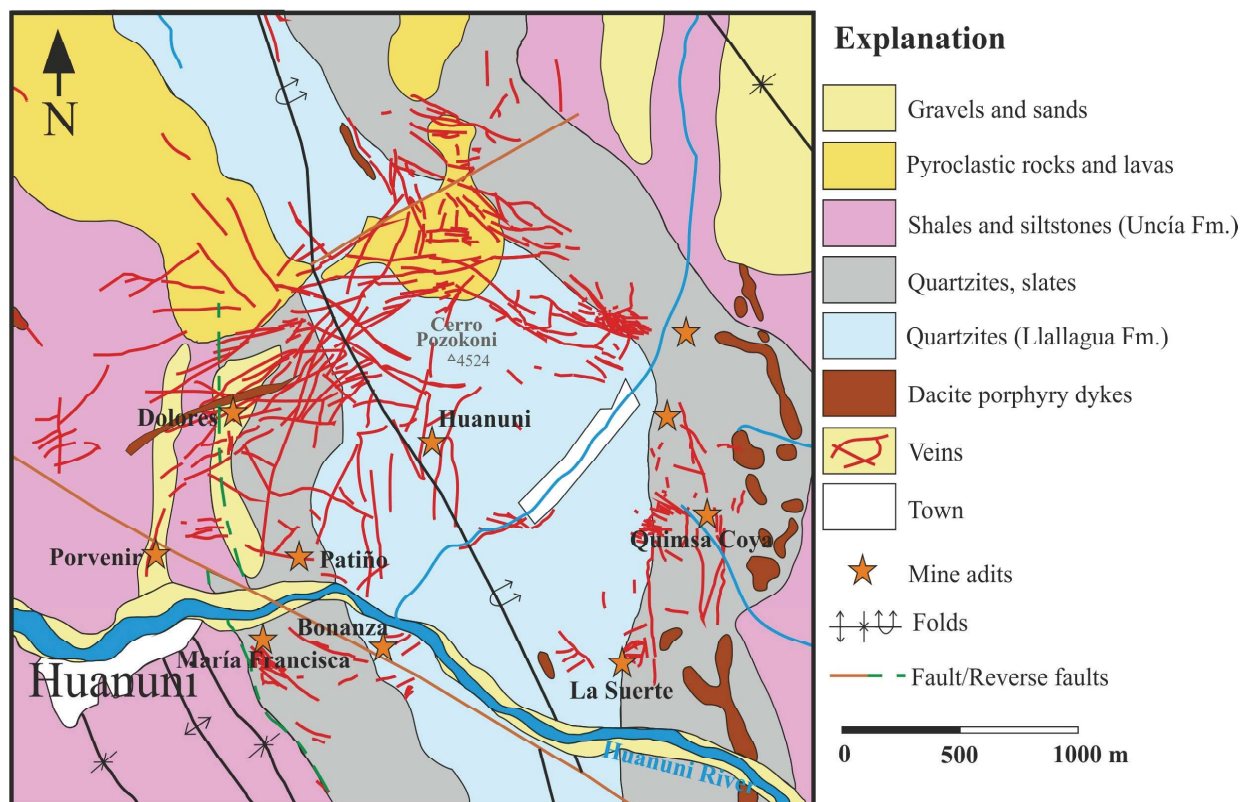


Figure 1. Photo-interpreted vein system (as in February 2015) in the Huanuni district. Geological base map after Arce (2009).

Nb or Ta (Möller et al. 1988; Ishihara et al. 2011; Hiroyasu and Shunsho 2013). However, detailed studies on their ore mineral geochemistry are scarce.

Here we present new mineralogy, ore mineral geochemistry and sulfur isotope data in order to better understand the Huanuni mineralizing system and the distribution and mobility of In.

2 Geological setting and structure of the deposit

The Huanuni district is located 275 km SE of the capital city La Paz, in the central part of the Eastern Cordillera of the Bolivian Andes. The Eastern Cordillera is composed of Ordovician to Cretaceous sedimentary sequences, comprising thick black shale, siltstone, limestone, sandstone, slate and quartzite layers (Fig. 1). The Andean orogeny produced regional fault and fold systems trending NNW-SSE (McQuarrie and DeCelles 2001). The ensemble is affected by low grade regional metamorphism. Intrusions of Miocene acid stocks and domes are mapped in the central part of the Eastern Cordillera, and they are partly covered by ignimbrite fluxes of upper Miocene age. To the east of the mining area, an ensemble of porphyritic dikes, trending approximately N-S, crops out along more than 1.5 km.

The mineralization is largely hosted in quartzites, shales and siltstones of the Uncía and Llallagua Formations and to a lesser extent in the pyroclastic and lava series of the Morococala Fm., of apparent Miocene age, around the Pozokoni hill (Fig. 1). The main structure at the deposit scale is the locally overturned Pozokoni anticline.

The polymetallic mineralization suite occurs as veins and infilling of the penetrative fault and fracture system developing around the Pozokoni anticline. New mapping of mined out veins cropping out along the district from recent detailed photo-interpretation is partially represented in Fig. 1. Mineralized veins of the Huanuni deposit form a conspicuously intricate and irregular framework; however, three main vein families are recognized following approximate directions of 1) 110° (e.g. Veta Grande, which is about 0.5 m thick; East, Nueva Chuallani or Progreso), 2) 160° (e.g. Norteña or Cruzera) and 3) between 045° and 080° (e.g. Esperanza and Amarilla).

3 Mineralogy and textures

The Huanuni district has been divided into two domains or zones: the central domain, with the Huanuni mine (Pozoconi Hill), and the distal domain, with the Bonanza and La Suerte mines.

3.1 Huanuni mine, central domain

Three stages of mineralization can be established from textural observations. In the first stage, the minerals fill open veins, and hence drusy quartz (deposited in all stages), along with a first generation of pyrite, cassiterite, arsenopyrite and pyrrhotite are largely idiomorphic with the exception of pyrrhotite.

During the second stage, a new generation of pyrite

and arsenopyrite with gersdorffite and cobaltite are deposited, followed by a sub-stage with schorl, chamosite and siderite; this second stage ends with the precipitation of native bismuth, wolframite (both ferberite and hübnerite) and a second generation of cassiterite, locally crystallizing as the needle tin variety.

The third stage is characterized by the precipitation of minerals such as stannite (Fig. 2A), sphalerite (showing systematic chalcopyrite disease), a third generation of pyrrhotite forming thin veins and finally sericite, acanthite and bismuthinite, frequently replacing the second-stage native bismuth.

3.2 Bonanza, distal domain

The sequence can be summarized into three stages of mineralization. During the first stage, euhedral quartz (which formed in all stages), pyrite and sphalerite (affected by chalcopyrite disease) deposited.

The second stage is recognized by a second generation of pyrite and rutile associated with cassiterite, sphalerite, an indium-rich carbonate (uncharacterized mineral species, Fig. 2B) and chamosite as alteration.

The third stage is characterized by a general Ag-enrichment, with the crystallization of galena accompanied by Ag-Cu-Sb-Bi-Te-sulfosalts such as freibergite, matildite, cervelleite and treasurerite, covered by siderite.

3.3 La Suerte, distal domain

The first stage of mineralization commences with the crystallization of quartz, whose formation continues throughout all stages of mineralization, and by a first generation of pyrite and acanthite, followed by the crystallization of idiomorphic crystals of arsenopyrite and sphalerite (affected by chalcopyrite disease).

During the second stage of mineralization, pyrite, rutile and cassiterite deposited, followed by a second generation of arsenopyrite, which replaced part of the existing pyrite.

Then, galena and sphalerite deposited accompanied by sericite; in this stage Ag-sulfosalts such as matildite, ferberite and pyrargyrite crystallized too.

Different phosphates such as fluorapatite, pyromorphite, monazite and plumbogummite (Fig. 2C) crystallized during a fourth stage and are common in this mine.

4 Mineral geochemistry

Mineral chemistry analyses were carried out by using EMP techniques at the *Serveis Científics i Tecnològics* of the Univ. of Barcelona and at the *Departamento de Geología* of the Univ. of Oviedo.

Cassiterite crystals from the central domain presented Nb and Ta contents mostly below their detection limits although concentrations up to 0.16 and 0.31 wt. % were detected.

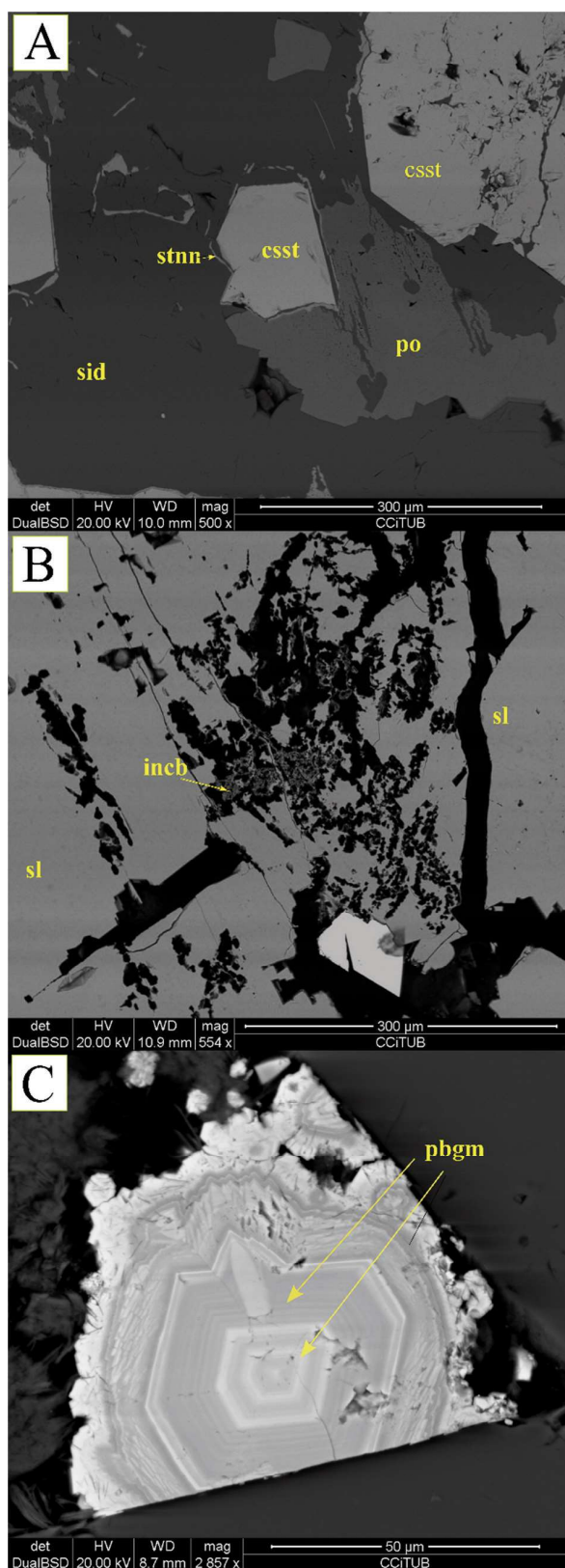


Figure 2. SEM-BSE microphotographs of Huanuni ores. **A.** Replacement of cassiterite (css) crystals by stannite (stnn) and pyrrhotite (po) and lately deposited siderite (sid) in Huanuni mine. **B.** Indium carbonate (incb) replacing indium-rich sphalerite (sl) in Bonanza mine. **C.** Zoned plumbogummite (pbgm) crystal from La Suerte mine; the zonation of the crystal is related to the lead contents.

Analyzed sphalerites have relatively high Fe contents of around 9.2 wt. %, although a few grains indistinctly from the two domains returned lower concentrations, as low as 0.5 wt. %. The concentration of Cd is in the range of 0.2 to 0.7 wt. %, and Mn is as high as 0.2 wt. %. Indium, commonly with concentrations under its detection limit, was detected only in mines from the distal domain; higher values were obtained in sphalerites from Bonanza, with concentrations between 0.05 to 0.8 wt. % whereas those from La Suerte mine returned In values up to 0.16 wt. %. Apparently, higher In concentrations in sphalerite systematically occur in those crystals which are free from chalcopyrite disease.

Analyzed stannite from the central domain presents a general structural formula $\text{Cu}_{1.83-1.96}(\text{Fe}_{0.94-1.14}, \text{Zn}_{0.01-0.14})\text{Sn}_{0.99-1.19}\text{S}_4$. Indium and Ge concentrations are as high as 0.12 and 0.13 wt. %, though they are largely under their detection limits.

5 Sulfur isotopes

A total of 30 analyses were performed on pure sulfur mineral grains (galena, pyrite, pyrrhotite and sphalerite) out of 20 rock samples in the *Serveis Científics i Tecnològics* of the University of Barcelona using a Delta C Finnigan MAT Delta-S mass spectrometer. $\delta^{34}\text{S}$ values are represented in the histogram in Fig. 3.

$\delta^{34}\text{S}$ values on sulfides from La Suerte and Bonanza mines (distal domain) are similar, tightly varying around 0 ‰. Sulfides from La Suerte returned $\delta^{34}\text{S}$ in the range of -4.2 to +0.8 ‰; however, the bulk of the analyses range from -1.8 to +0.8 ‰. Lowest values were registered in sphalerite grains (-4.2 and -3.3 ‰). Sulfide grains from Bonanza mine returned $\delta^{34}\text{S}$ values between -1.3 to +0.5 ‰.

$\delta^{34}\text{S}$ values of analyzed sulfides from the Huanuni mine (central domain) are in general more negative, with values ranging from -7.5 ‰ to -4 ‰, although three pyrite grains returned $\delta^{34}\text{S}$ in the range of -2 to +0.5 ‰.

6 Discussion and conclusions

6.1 Mineralogy and distribution of indium

Mineral paragenesis here described for ores from the Huanuni mine (central part of the district) is indicative of a continued drop in the mineralizing fluid temperatures. In contrast, the paragenetic sequences described in the distal domain (Bonanza and La Suerte mines) is suggestive of a complex mineralizing process and robustly suggests an increase and a subsequent drop in the temperature of the mineralizing fluids. Telescoping and consequent overlapping of polymetallic mineralizations formed at different physico-chemical conditions is a plausible explanation longly ago interpreted for the neighboring Lallagua deposit (Bandy 1942).

Sphalerite and stannite from the proximal and distal domains returned conspicuously low Ge contents, whereas Ga was never detected. Although steadily low, In concentrated preferably in sphalerite crystals from the

distal domain, probably linked to precipitation of the second (lower temperature) generation of sphalerite (chalcopyrite disease-free). Higher In contents in Bonanza mine correlates with the occurrence of an uncharacterized In-carbonate mineral specie.

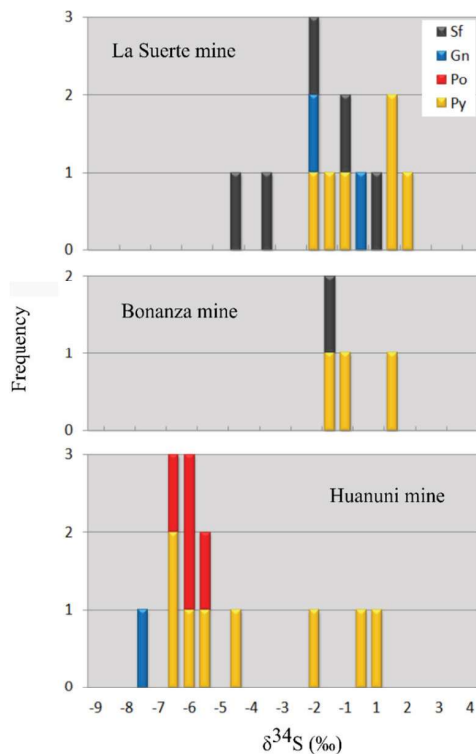


Figure 3. Histogram of $\delta^{34}\text{S}$ values of analysed sulfide grains. Sf: sphalerite; Gn: galena; Po: pyrrhotite; Py: pyrite.

6.2 Constraints from sulfur isotope data

$\delta^{34}\text{S}$ values can be roughly gathered into two groups. The first contains values around the 0 ‰ (distal domain), whereas the second contains values among -8,0 and -3,0 ‰ (central domain). These results reflect a sulfur isotopic zonation at the district scale.

Ishihara (1981) was the first to establish that the mineralization of magmatic-hydrothermal deposits was strongly influenced by the magmatic series (granitoids) of the genetically related magmas. Hypogenic Sn and W deposits are generally associated to ilmenite-series magmatism and more specifically to S-type magmas of crustal origin, as stated in the Bolivian Sn and W deposits (Redwood 1993). According to Ohmoto and Goldhaber (1997), the extremely reducing character of S-type magmas translates into outstanding dominance of H_2S sulfur specie in magmatic fluids (at $P_{\text{H}_2\text{O}} > 100$ bar). As fractionation factor between H_2S and S_2^- species dissolved in magma is negligible, $\delta^{34}\text{S}_{\text{S}}$ value will be, in the main, identical to that of the magmas.

Ohmoto and Golhaber (1997) postulated that, in porphyry deposits related with S-type granitoids, the source of S^{2-} to precipitate the sulfides derives basically from magmatic fluids that acquired most of their sulfur through assimilation from the local country rocks. Hence, variations of $\delta^{34}\text{S}$ in a deposit is commonly

attributed either to different grades of selective assimilation of the hosting rock sulfur during the fractionated crystallization of the magma and/or the interaction with external fluids (e.g. Wagner et al. 2009).

Assuming a migration of the mineralizing fluid from the central part (tin porphyry) of the deposit towards the periphery (polymetallic), interaction with oxidizing rainwater or groundwater giving sulfur-sulfate co-precipitation would have resulted in progressively lower values of $\delta^{34}\text{S}$; this mechanism is, consequently, ruled out in our study case. In contrast, variable grade of assimilation of sulfur from the hosting rocks during the emplacement and cooling of a single acid stock or a multi-episodic intrusive history is contemplated. Further work, including the sulfur isotopic characterization of sulfides in the hosting sedimentary sequence and stocks is currently under way.

Acknowledgements

The Corporación Minera de Bolivia (COMIBOL) allowed us to visit and sample the mines. Funding was provided by the 2014-SGR-1661 (Generalitat de Catalunya) and the AECID A3/042750/11 projects.

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