Mineralogical Characterization of Sn Deposits from the Santa Fe District, Bolivia

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Abstract. The Sn-Zn-Pb-Ag Japo-Santa Fe-Morococala ore deposit is located in the Central Andean Belt province. The ore mineralization is hosted in a Paleozoic metasedimentary sequence and porphyritic Oligocene-Miocene igneous rocks. Ore minerals occur in veins and disseminations. Two types of ore mineralization are distinghished: (1) An early Sn mineralization and (2) a late Sn and Zn-Pb-Ag mineralization. Mineral association consists mainly of quartz, pyrite, cassiterite, other sulfides and sulfosalts. Cassiterite, up to 0.25 wt% In, constitutes the earliest mineralization. Galena and sphalerite are the main sulphide minerals. Sphalerite shows up 0.24 wt% In. Stannite group is represented by stannoidite, kësterite, and sulfides of the Sn-Cu-Zn-Fe-S system. Sulfosalts include sakuraiite, potosiite, franckeite, freibergite, tetrahedrite, myargyrite, boulangerite, jamesonite, zinckenite, cylindrite and andorite. In this deposit, after an epigenetic magmatic stage, a long greisen-hydrothermal event took place with several episodes of metal deposition.

Keywords. Tin, sulfosalts; stannite; indium, Bolivia

1 Introduction

The central Andean Belt is an important tin province which allows many world-class deposits (e.g. Cerro Rico, Llallagua and San José). This belt extends along of approximately 900 km to the northwest in the Eastern Cordillera of Bolivia.

The genesis and characteristics of some of these deposits have been poorly studied so far. However, these ore deposits arouse great interest by their high content in indium (Ishihara et al. 2011; Murakami and Ishihara 2013), which is considered as a strategic metal.

This is the case of the Sn-Zn-Pb-Ag Santa Fe mining district, located in the Oruro department. This district comprises three areas: Japo, Santa Fe, and Morococala, which are being mined for Sn, Zn, Ag and Pb. Only the regional geological characteristics of this area were reported (Sugaki et al. 1981).

In the present work we present the geology and mineralogical and mineral chemistry data of the Japo-Santa Fe-Morococala ore deposit.

2 Geological setting

The tin mineralization in the Santa Fe district (Fig. 1) is spatially related to intrusive bodies, consisting of peraluminous granites and porphyry intrusions of different pulses, being the most widespread of Oligocene-Miocene age (Grant et al. 1979). The Amutara Fm is a Palaeozoic metasedimentary sequence. It is the basement of the stratigraphic sequence, which is a shale and sandstone turbidite deep marine unit. This unit is overlaid by a Silurian sequence of the Cacañiri, Llallagua and Uncia formations. The Cancañiri Fm. covers the Amutara unit, and it is constituted by micaceous sandstones and siltstones that gradually change to quartzites, sandstones, siltstones and grey-green shales of the Llallagua and Uncia formations. The Silurian sequence ends with the Uncía Fm, which is conformed by shales and sandstones. An intense tectonic activity in different periods of time folding and thrusting this sequence. These materials are unconformably covered by the volcanic complex of the Morococala Fm., mainly constituted by calc-alkaline lavas and tuffs of Miocene age (Sugaki et al. 1981).

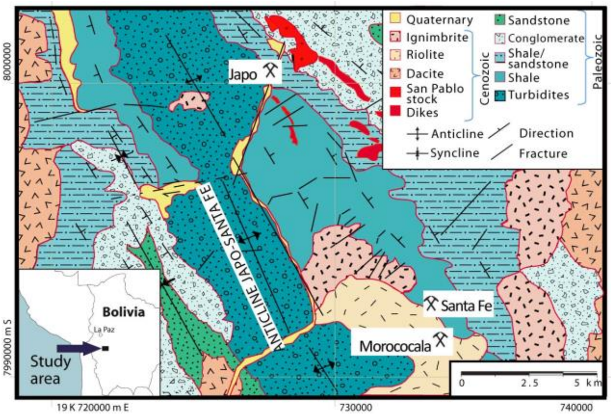

Figure 1. Geological map of the study area.

Mineralization in Santa Fe and Morococala occurs as veins and disseminations. A wide N40º shear zone and two fracture systems are developed: a N40º one, dipping 60ºW, which hosts Sn and Zn ores, and another in the same direction but dipping 75ºE, to which the Zn-Pb-Ag veins are related . The mineralization is associated with felsic magmatism, represented by several generations of dykes and the felsic San Pablo stock, which is located near to the Japo mine.

3 Mineralogy and mineral chemistry

Both country rocks and ore mineralization were sampled in Japo, Santa Fe and Morococala mines and outcrops. Additionally, 5000 m of drill cores from the Japo mine were examined and sampled. Mineralogy of the samples was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA).

Two stages of mineralization can be distinguished: (1) Early, Sn-rich mineralization, represented by cassiterite; and (2) late, sulfide mineralization, represented by sphalerite, galena and minerals of the stannite group. Cassiterite mineralization predominates in the Japo ore deposit, while, in Santa Fe and Morococala different generations of Sn and Zn-Pb-Ag mineralization are found.

3.1 Host rocks

Ore mineralization is mainly hosted in the metasedimentary sequence. It preferably occurs in the lithological and structural contacts. Ores occur as replacements and as porosity and fractures infillings.

Intrusive and porphyritic bodies show a pervasive argillic alteration. They have a porphyritic texture, with phenocrystals of quartz, feldspar, micas and tourmaline, many of which are replaced by sulfides, chlorite and epidote. The alteration is more intense along the contact between host rocks and veins. Alteration minerals are mostly sericite, alunite, plumbojarosite, kaolinite, vermiculite and dickite.

3.2. Ore minerals

Veins are filled with quartz and pyrite an ore assemblage of cassiterite, other sulfides and sulfosalts. Among the supergene minerals gypsum, calcite, melanterite and vivianite ($Fe^{3+}(PO_4)_2 \cdot 8H_2O$) can be mentioned. Rutile is associated with of the latest cassiterite and forms needle-like crystals.

Cassiterite constitutes the earliest stage of mineralization in association with pyrite, arsenopyrite, chalcopyrite and chalcocite. Preliminary EPMA analyses indicate that cassiterite has high concentrations of In, between 0.12 and 0.25 wt.%. The Ta and Nb contents are negligible.

Galena and sphalerite are the most abundant sulfides. Galena is commonly associated with sulfosalts. EPMA analyses reveal an average of 0.30 wt.% Ag in galena. Vianeite is also present, (structural formula ($(Fe_{3.8}Pb_{0.3})_4S_8O$).

Microprobe analyses of sphalerite, show indium contents up to 0.24 wt%. Similar values have been reported for sphalerite from the Potosi and Huari huari deposits of the central Andean belt (Murakami and Ishihara 2013). In addition, sphalerites from polymetallic veins reported by Seifert and Sandmann (2006) also show similar In contents. Sphalerite has a negative correlation between Fe+Cd+In and Zn, indicating a ion substitution among these metals (Fig. 2).

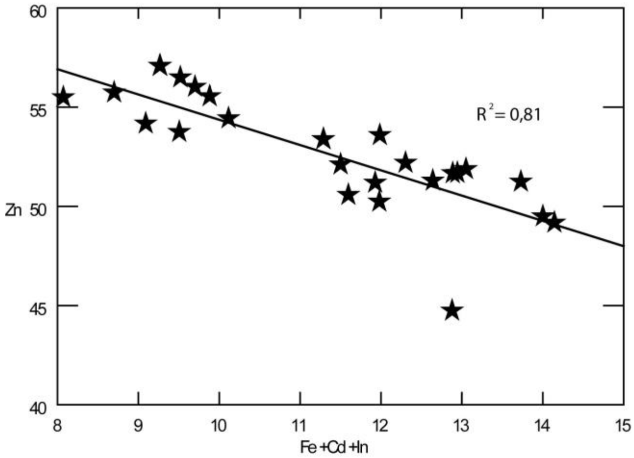

Figure 2. Fe+Cd+In vs. Zn plot in sphalerite from the Santa Fe district.

Sn is also present in sulfides as stannite, stannoidite kësterite, and sulfides of the S-Sn-Cu-Zn-Fe- system. Stannite occurs filling cavities and within the cleavage in primary mineral, in association with quartz and pyrite. Stannite from Japo and Morococala is rich in In, up to 0.2 wt %, whereas that of Santa Fe is depleted in this element (Fig. 3b,c).

Stannite is called for Fe>Zn phases, and kësterite for Zn>Fe (Hall et al. 1978). We estimated stannite structural formula as ($Cu_{1.6}(Fe_{0.9}\ Zn_{0.7})Sn_{0.8}S_4$) and kësterite ($Cu_{1.5}(Zn_{1.1}\ Fe_{0.9})Sn_{0.7}S_4$)

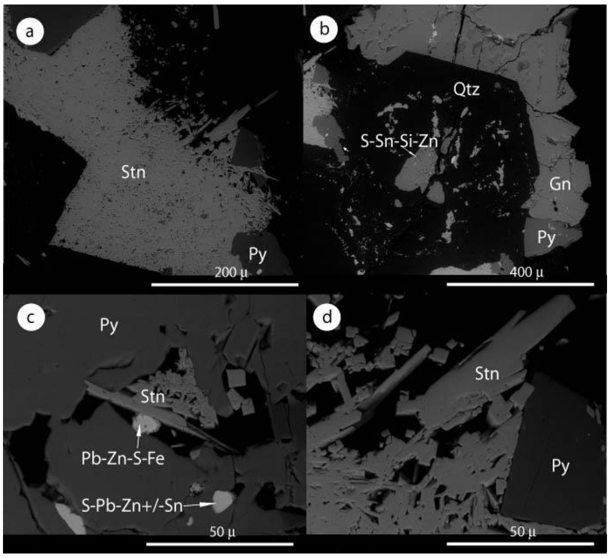

Figure 3. Backscattered SEM images of (a) Stannite crystals with pyrite (b) Ore minerals associated to euhedral quartz; (c) minerals of stannite group with composition variable, (d) stannite prismatic crystals associated with pyrite. Key: Qtz, quartz; Py, pyrite; Gn, galena; Stn, stannite.

Pirquitasite is an Ag- and Sn-rich sulfide that occurs in Santa Fe with the structural formula ($Ag_{1.9}Sn_{1.0}Fe_{0.3}S_4$).

Exceptionally, some sulfide minerals contain Si in variable amounts (Fig. 3d). These measurements were performed in absence of Si-rich minerals close the spot analyses. Other sulfides present are pyrrhotite, stibinite, marcasite and argentite.

Sulfosalts include several Sn-rich members as potosiite ($Pb_{6.1}Sn_{2.6}Fe_{1.8}Sb_{2.3}S_{15.7}$) and franckeite ($(Pb_{5.6}Sn_{2.4})Sn_{2.}Fe_{1.0}Sb_{2.0}S_{14}$). Other sulfosalts are Ag-rich, as freibergite (up to 14.95 wt % Ag), tetrahedrite, myargyrite, boulangerite, jamesonite, zinckenite, cylindrite and andorite. Bismuthinite and berndtite are found in trace amounts.

3.3 Phosphate minerals

Phosphates occur in cavities and small fractures in two different stages: a) first, during a late magmatic stage monacite $(Ce,La,Nd,Th)PO_4$ was formed and b) as plumbogummite ($PbAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$) during a late, supergene stage of the ore deposit. Crandallite $CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$ also occur in minor amounts.

4 Discussion and conclusions

Textural analysis suggests an epigenetic mineral deposition formed by a multistage event. The sequence of crystallization of the mineralization is shown in Fig. 4. Four main paragenetic stages can be inferred, from old to young: (1) Magmatic stage and injection of hydrothermal fluids rich in metals, especially in Sn; (2) metasomatism producing the alteration of meta sedimentary sequences, synchronous to late magmatic stage; (3) late hydrothermal stage with sulfide deposition; and (4) supergene alteration that formed a complex, replacive paragenesis rich in phosphates.

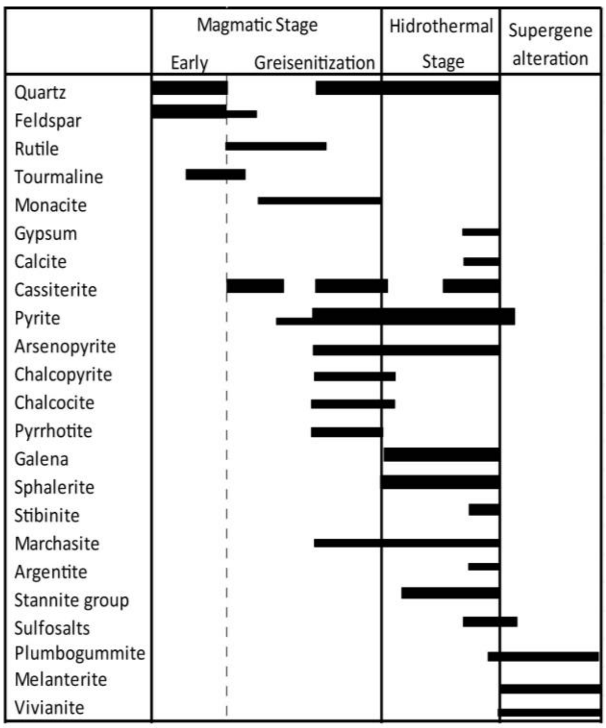

Figure 4. Paragenetic sequence of the Japo-Santa Fe-Morococala tin deposit.

The ore-hosting rocks in these deposits are intrusive and metasedimentary rocks. The former have an association of quartz-feldspars-micas, accompanied by variable amounts of rutile and tourmaline. Burt (1981) defined greisen as hydrothermally altered granitic rocks consisting of an association of quartz and micas with variable topaz, tourmaline and fluorite or other F- or B-rich minerals. Greisen result from complex metasomatic processes that affect and take place within a nearly granitic mass and the adjacent country rocks (Pirajno, 2009) and are commonly associated to Sn mineralization. In this deposit, after the magmatic stage, a mineralizing event took place due the interaction between the metasedimentary rocks and metal-rich hydrothermal fluids. This stage presented several episodes of metal deposition forming veins or filling discontinuities as lithological contacts or shear zones. This stage was the most important for ore mineralization. Thereafter, a later stage of supergene alteration took place.

The geochemical composition of these minerals suggests a complex solid solution between In-rich stannite-kësterite and sulfosalts. According to Shimizu et al. (1986), stannite-kësterite composition shows substitutions of (Zn,Fe) In for CuSn, which is consistent with this study results. Fig. 5 illustrates these compositional variations, which has an S-Cu-Fe-Sn-In-stannite-kësterite trend.

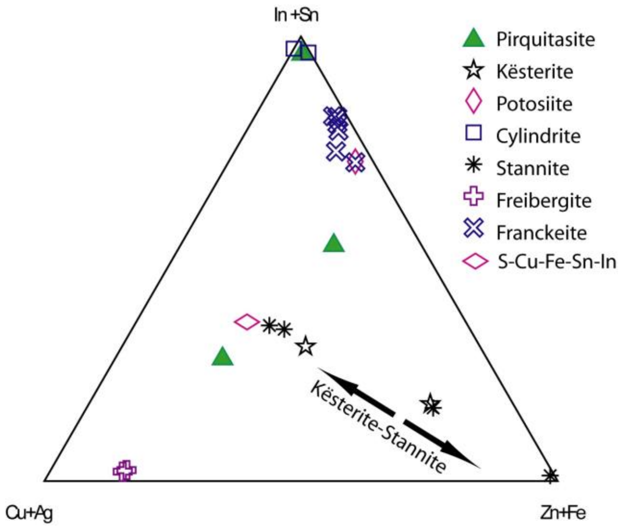

Figure 5. Ternary Cu+Ag–Sn+In–Zn+Fe plot of indium-rich minerals from Japo and Santa Fe mines.

Indium concentration in tin minerals shows anomalously high values, so that further analyses are necessary in order to assess the importance of this strategic element in the deposit.

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