

Distribution of indium in the Ánimas – Chocaya – Siete Suyos District

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Abstract. The Ánimas – Chocaya – Siete Suyos district in SW Bolivia hosts a Bolivian-type polymetallic vein mineralization composed mostly of cassiterite, sphalerite, pyrite, galena, stannite, lead sulfosalts, tin sulfosalts and silver sulfosalts. In addition to base (Zn, Sn, Pb) and precious (Ag) metals, important concentrations of In have been described. Systematic EPMA analyses have revealed that the highest concentrations are found in an early generation of sphalerite (up to 9.66 wt% In) and in stannite (up to 4.11 wt% In). Although In-bearing sphalerites are relatively Fe-rich (mostly between 6.0 and 18.1 mol % FeS), the atomic concentrations of these two elements do not yield any correlation. In contrast, In is positively correlated with Cu mostly along a Cu/In = 1 proportion pointing to a $(\text{In}^{3+} + \text{Cu}^{+}) \leftrightarrow 2\text{Zn}^{2+}$ coupled substitution. A relatively high activity of Cu during the crystallization of In-rich sphalerite is also supported by exsolutions of chalcopyrite and stannite.

1 Introduction

Indium (In) is currently considered a critical raw material because of its high market demand coupled to a high supply risk (European Commission 2017; Schulz et al. 2017). It is an essential component in modern technologies such as flat touch panels (as indium-tin oxide – ITO) and in the so-called green technologies such as photovoltaic cells. There are not mines that host indium as a primary commodity. This technological element, and others such as Ge, are mostly recovered as by-products from the production of other metals, chiefly zinc in sulfide minerals (i.e., sphalerite) even if important resources are described in tin ore as well (Schwarz-Schampera and Herzig 2002).

Important concentrations of In are described in the metalliferous belts in the Central Andean region (Fig. 1), particularly in the Andean tin belt (Schwarz-Schampera and Herzig 2002; Ishihara et al. 2011; Murakami and Ishihara 2013).

Mines in the Ánimas - Chocaya- Siete Suyos district are currently operated by several mining cooperatives.

Ishihara et al. (2011) studied the concentration of trace metals in 5 composite ore samples from Siete Suyos and Ánimas mines and reported whole rock In concentrations as high as 2510 ppm. Nevertheless, ore mineral chemistry has not been reported previously for this district and the mineralogical expression of In is hence unknown.

Here we present new data on the mineralogy and ore mineral geochemistry, with a particular focus on the critical metal In, to better understand its distribution at the district scale and along the paragenetic sequence.

2 Materials and methods

A total of 50 samples were examined for mineralogical and geochemical determinations. The distribution of the samples embraces the three deposits and for each, several veins and mining galleries at different depths in order to ensure a complete 3D representability at the district scale.

Forty polished thin and thick sections have been studied by optical and scanning electron microscopy (SEM) using an environmental Quanta 200 FEI, XTE 325/D8395 equipment with an INCA Energy 250 EDS microanalysis system at Centres Científics i Tecnològics of the University of Barcelona (CCiT-UB).

Mineral chemistry analyses of sulfide minerals and cassiterite were performed using a five-channel JEOL JXA-8230 electron microprobe (EPMA) at the CCiT-UB, operated at 20 kV acceleration voltage, 20 nA beam current, with a beam diameter of 5 μm .

3 Geological setting

The Ánimas – Chocaya – Siete Suyos district is located in the Potosí Department, 150 km south of the city of Potosí and near the town of Atocha. Physiographically, it sits in the western flank of the Eastern Cordillera, close to the Altiplano. The Eastern Cordillera is composed mostly of thrust, folded and variably metamorphosed Paleozoic marine sedimentary rocks, overlain by marine and non-marine Cretaceous

sedimentary rocks (Suarez-Soruco 2000).

The district is included in the Quechisla mining group and belongs to the Andean (or Bolivian) tin belt, one of the metalliferous belts distinguished in the Central Andes (Fig. 1; cf. Mlynarczyk and William-Jones 2005; Fontboté 2018). The Andean tin belt is confined to the Eastern Cordillera and extends along more than 1000 km from southern Peru to northern Argentina through Bolivia. In this belt, mineralization was triggered by reduced, peraluminous magmatism. In its southern portion, where the Ánimas – Chocaya – Siete Suyos district is located (Fig. 1), Sn, Sn-W and Sn-polymetallic mineralization is of late Oligocene and Miocene age (Arce-Burgoa 2009) and related to porphyritic intrusions and dome complexes including hydrothermal breccia pipes and collapse calderas (Heuschmidt et al. 2002; Arce-Burgoa 2009).

Mineralization in the Ánimas – Chocaya – Siete Suyos district is genetically associated to the Chocaya volcanic caldera complex of Miocene age (ca. 14–12 Ma; Heuschmidt et al. 2002). A lava and pyroclastic pile of dacitic composition is protruded by a central dome of the same composition. The volcanic complex is hosted by Ordovician sandstones and slates.

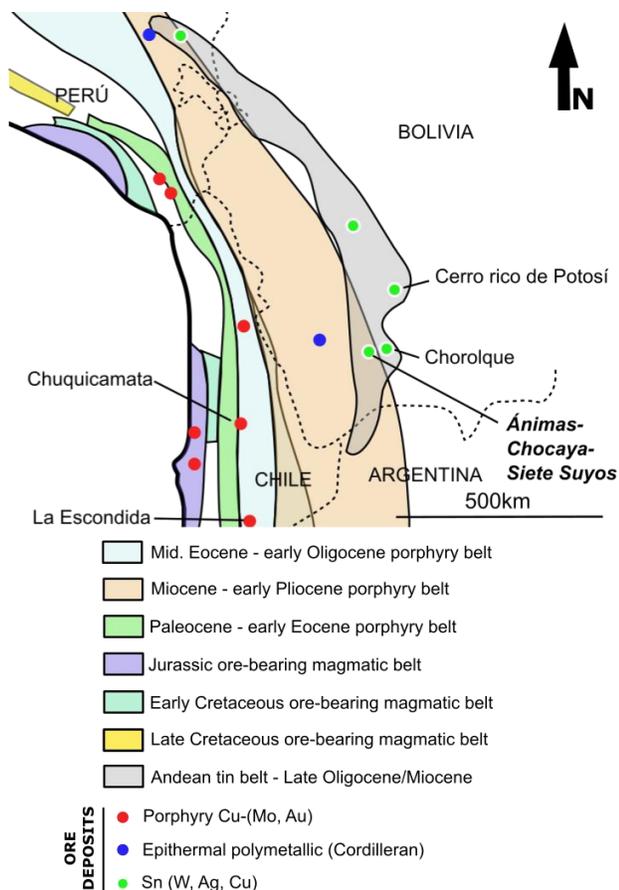


Figure 1. Schematic map of the Central Andes with the main mineralized belts and representative ore deposits. Modified from Fontboté (2018).

Volcanic and basement metamorphosed sedimentary rocks are crosscut by a NE-SW oriented network of

veins that extends for more than 5 Km from the Siete Suyos mine (to the NE) to the Chocaya mine (to the SW); some veins have been exploited to depths of ~900 m (e.g., Burto and Colorada veins).

4 Mineralogy

The district has a zoned distribution of the ores, with a complex ore association in the central parts of the district, particularly at depth (Figs. 2–5), and chalcedony-barite veins, with lesser amounts of galena and sphalerite, in the marginal parts of the district.

The main ores in the central part of the district are sphalerite, pyrite and galena, accompanied by a gangue largely composed of quartz and siderite, with minor proportions of apatite, zircon and Al-rich phosphates. Other important phases usually found in the central and deep part of the mineralization include cassiterite, pyrrhotite, arsenopyrite, stannite, chalcopyrite and tetrahedrite.

Minor phases scattered in the central part of the deposit, which may account for most of the silver content, include native silver, acanthite and silver-rich sulfosalts such as miargyrite, oscarkeppfite, owyheeite, andorite, diaphorite, pyrargyrite, terrywallaceite, franckeite, staročeskéite and zoubekite; in addition, minor amounts of jamesonite, boulangerite, heteromorphite, semseyite, stibnite, wolframite, scheelite, and wurtzite also occurs.

Supergene products include minerals of the jarosite group, goethite, anglesite and smithsonite.

Hydrothermal alteration of the host rocks consists largely of silicification accompanied with argillic and sericitic alterations in the central part of the district, and a propylitic halo with abundant chlorite at the margins.

5 Textures and paragenetic sequence

Vein infilling shows drusy or cockade growths of quartz and ore, often displaying banding or colloform arrangements, suggesting open space crystallization. In addition, late minerals may also occur as veinlets that crosscut earlier phases. Different generations of a same mineral species are revealed by changes in the textural patterns. Some minerals, in particular pyrite, arsenopyrite and sphalerite, show oscillatory zoning.

Early phases in the studied veins include quartz, cassiterite, arsenopyrite, a first generation of sphalerite, stannite and pyrite (Fig. 2). Cassiterite crystallized synchronously with quartz, even if the later formed during most of the mineralization lifespan in variable amounts. Arsenopyrite is largely replaced by pyrite suggesting a general earlier precipitation (Fig. 3). Sphalerite, the chief ore mineral in the district, probably crystallized during a protracted period. Early sphalerite is observed to form colloform bands overgrowing quartz and arsenopyrite, and by hosting myriads of chalcopyrite and stannite exsolutions. The abundance of these exsolutions decreases toward inner, younger sphalerite bands giving way to interspersed bands with stannite (Fig. 2). Later generations of sphalerite are largely free

of both chalcopyrite and stannite exsolutions and intergrowths with stannite (Fig. 4). Galena is observed mostly as anhedral grains often replaced by late sphalerite (Fig. 5). Chalcopyrite is rather scarce in the studied ore and, in addition to forming exsolutions in sphalerite, is observed veining this mineral (Fig. 4), suggesting later crystallization.

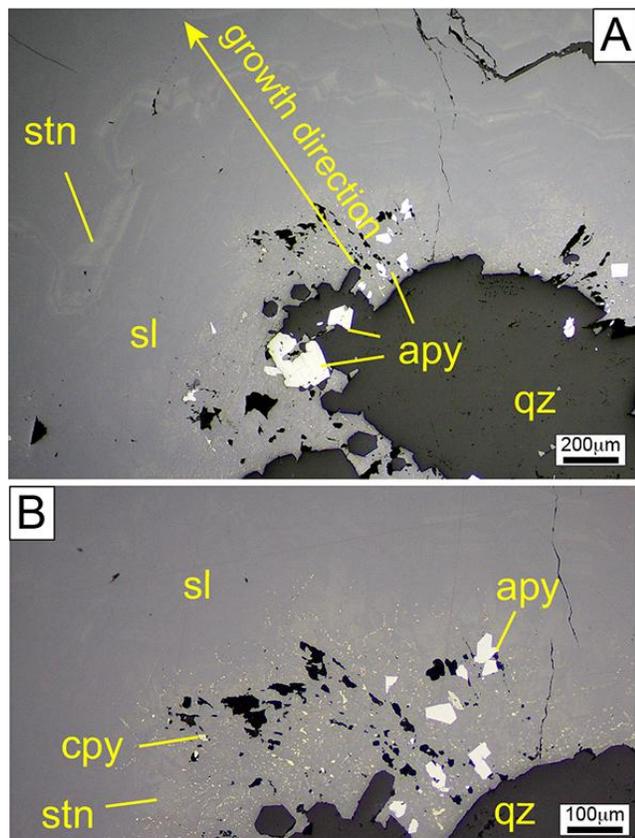


Figure 2. Microphotographs of ore mineralization from the Siete Suyos mine using reflected, plane polarized light. A) Colloform growths of sphalerite (sl) bands interspersed with stannite (stn) bands overgrew quartz (qz) and arsenopyrite (apy). B) The density of exsolutions of stannite and chalcopyrite (cpy) in sphalerite decreases toward younger growth bands.

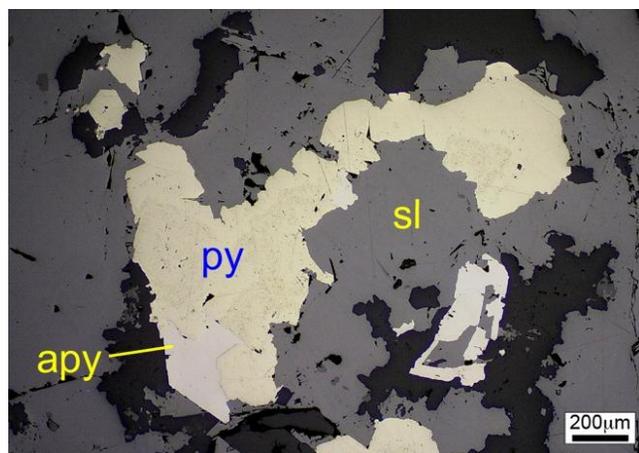


Figure 3. Arsenopyrite (apy) crystals were extensively replaced by pyrite (py), and both were replaced by a late generation of exsolution-free sphalerite (sl) in ore from the Siete Suyos mine (reflected, plane polarized light).

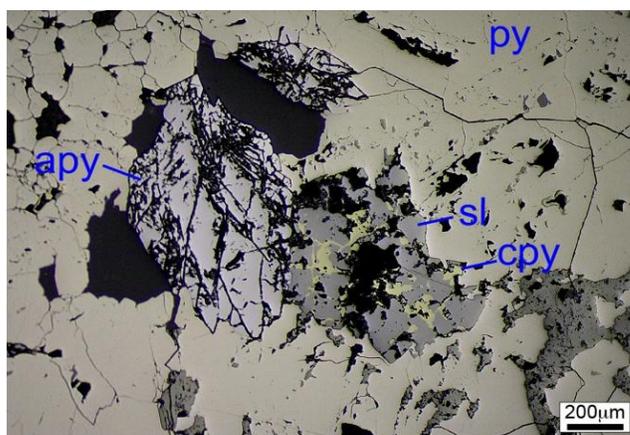


Figure 4. Arsenopyrite (apy) crystal replaced by pyrite (py), the second replaced in turn by sphalerite (sl). Chalcopyrite (cpy) veins sphalerite (sample from the Animas mine; reflected, plane polarized light image).

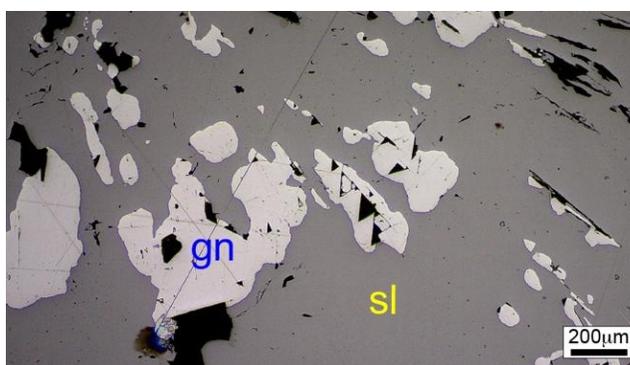


Figure 5. Galena (gn) grains are conspicuously replaced by a later generation of exsolution-free sphalerite (sl) in ore from the Animas mine (reflected, plane polarized light image).

Later phases include sulfosalts, mostly tetrahedrite (locally found in equilibrium with a second generation of stannite) and Pb sulfosalts that are almost synchronic with the crystallization of Ag sulfosalts. These phases crystallized in equilibrium with late sphalerite and a second generation of galena and Fe-carbonates (Fig. 6) In a few samples, late wurtzite has been identified.

Mineral	Early	Late
Quartz	████████████████████	████████████████████
Casiterite	████████████████████	████████████████████
Arsenopyrite	████████████████████	████████████████████
Pyrite	████████████████████	████████████████████
Sphalerite	████████████████████	████████████████████
Stannite	████████████████████	████████████████████
Galena	████████████████████	████████████████████
Chalcopyrite	████████████████████	████████████████████
Tetrahedrite	████████████████████	████████████████████
Pb/Ag sulfosalts	████████████████████	████████████████████
Fe-carbonate	████████████████████	████████████████████

Figure 6. General, simplified paragenetic sequence of hypogene mineralization in the Animas and Siete Suyos mines.

6 Geochemistry of In-bearing ore minerals

Remarkable concentrations of In have been detected only in sphalerite and stannite. Contrasting compositions for sphalerite have been observed depending on the generation or in the vein system in which they crystallized. First-generation sphalerite is characterized by the highest In concentrations (up to 9.66 wt% in a sample from the Siete Suyos mine, up to 2.94 wt% in a sample from the Ánimas mine and up to 1.82 wt% in a sample from the Chocaya mine). In Siete Suyos and Ánimas ore, In-bearing sphalerite crystals are characterized by high Fe contents so that for sphalerite grains with In > 1.5 wt%, FeS is between 6 and 18 mol % in the Siete Suyos mine, and between 8 and 16 mol % in the Ánimas mine. In contrast, for sphalerite grains from the Chocaya mine with In > 1 wt%, the concentration of Fe is low, between 0.1 and 0.3 mol % FeS. A correlation between atomic proportions of In and Fe is not observed. In contrast, the atomic proportions of In yield a strong positive correlation with those of Cu, mostly at Cu/In=1. Some of the studied sphalerite grains yield a limited solid solution with stannite (up to 4 mol % Cu₂FeSnS₄).

Studied stannite yields a maximum content of In of 4.11 wt% in a sample from the Ánimas mine, whereas maximum concentration in stannite grains from the Siete Suyos mine is of 1.73 wt%. The concentration of In in stannite does not show clear correlation with other analyzed elements.

Analyzed cassiterite crystals yield only minor concentrations of In, up to 0.65 wt%.

7 Discussion

The strong correlation found between Cu and In in sphalerite grains from the Ánimas – Chocaya – Siete Suyos district at Cu/In=1 points to incorporation of In via a (Cu⁺ + In³⁺) ↔ 2Zn²⁺ coupled substitution, which has been amply identified in other districts worldwide for In-bearing sphalerite (Cook et al. 2011, and references therein). On the other hand, the occurrence of In in studied stannite favors a contextualization of the In mineralization in the (Zn,Fe)S – Cu₂FeSnS₄ – CuInS₂ pseudoternary system described by Oen et al. (1980), with a limited solid solution between the three endmembers (i.e., sphalerite, stannite and roquesite). The fact that In strongly correlates with Cu in the structure of sphalerite and is systematically found in first-generation sphalerite texturally characterized by hosting abundant chalcopyrite and stannite exsolutions suggests that Cu played a major role in the concentration of In. In contrast, the concentration of Fe in sphalerite is apparently disconnected of the initial concentration of In in this mineral. Nevertheless, high concentrations of FeS in sphalerite are described to favor diffusion of elements such as In in the structure of this sulfide and hence might have promoted local diffusion fronts enriched in roquesite solid solution (Schwarz-Schampera and Herzig 2002).

Acknowledgements

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