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Trace elements of Indium-bearing sphalerite from tin-polymetallic deposits in Bolivia, China and Japan: A femto-second LA-ICPMS study

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ARTICLE INFO

Article history: Received 24 August 2012 Received in revised form 16 January 2013 Accepted 17 January 2013 Available online 31 January 2013

Keywords: Indium Sphalerite Tin-polymetallic deposit Femto-second LA-ICPMS Jamesonite Coupled substitution Magnetite-series granitoid

ABSTRACT

Indium-bearing tin-polymetallic base metal deposits in Japan (Toyoha, Ashio and Akenobe), China (Dulong and Dachang), and Bolivia (Potosi, Huari Huari, Bolivar and Porco), were studied using femto-second Laser Ablation ICPMS (fsLA-ICPMS) and EPMA analyses for major and minor elements in sphalerite, paying special attention to In concentrations.

Sphalerite is a principal mineral in these tin-polymetallic deposits and a broad range of In concentration is measured in the ores. There are distinct differences in mode of occurrence of the sphalerite and the distribution of In. The highest In concentration (up to 18 wt.%) occur as a Zn–In mineral within black sphalerite zones in an oscillatory-zoned sphalerite from the Huari Huari deposits. Additionally, jamesonite from the Huari Huari deposit also contains anomalous In values, ranging from several hundreds to thousands µg/g. Sphalerite from the Toyoha and the other Bolivian deposits are characterized by oscillatory and chemical zoning, whereas those from Akenobe and the Chinese deposits are represented by homogeneous distribution of In. The 1000In/Zn values of sphalerite are in good agreement with those of the ore grade for each of the selected tin polymetallic deposits indicating that sphalerite is the principal host of In.

The In-bearing sphalerite principally involves the combined coupled substitutions $(2Zn^{2+}) \leftrightarrow (Cu^+, In^{3+})$, $(3Zn^{2+}) \leftrightarrow (Cu^+, Ag^+, Sn^{4+})$ and $(3Zn^{2+}) \leftrightarrow (2Cu^+, Sn^{4+})$. The first of these is apparent in sphalerite from Huari Huari and Bolivar, whereas the second is prominent in sphalerite from Toyoha, Ashio, Potosi, Porco and Dachang. Akenobe and Dulong sphalerite features the dominant coupled substitution of $(2Zn^{2+}) \leftrightarrow (Cu^+ \text{ or } Ag^+, In^{3+})$, owing to their poor Sn content. Occasionally, sub-micron inclusions of minerals such as stannite and Pb-Sb-bearing sulfides can occur in sphalerite, contributing to high Cu–Sn and high-Ag contents, respectively. The observed correlations of each element in the In–Cu–Ag–Sn-bearing sphalerite can be proposed as a fundamental reason for the indium enrichment related to sulfur-rich oxidized magmatism. In addition, the Ag content in sphalerite is considered a possible indicator of formation depth, which ranges from plutonic to subvolcanic environments.

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1. Introduction

Indium is recovered as a by-product of zinc processing from a number of zinc deposits, but is nevertheless one of the crucial elements for a wide variety of high technology applications. Indium is economically exploited from two primary sources, massive sulfide deposits (Fig. 1; Benzaazoua et al., 2003; Schwarz-Schampera and Herzig, 2002) and tin-polymetallic-zinc deposits (hereafter tin polymetallic deposits) of vein and fissure filling-types in various geological terrains in China (Zhang et al., 1998), Japan (Imai et al., 1975; Ishihara et al., 2006; Ohta, 1989), and Bolivia (Ahlfeld, 1967; Grant et al., 1980; Ishihara et al., 2011b; Sillitoe et al., 1975; Sugaki et al., 1988b; Turneaure, 1960). Previous studies addressing tin-polymetallic deposits speculated upon potential indium resources by analyzing the In contents in the ore components within exploited and remaining ores in several regions of the world. For instance, they indicate total amounts of indium are estimated about 11,000 tons in southern China (Ishihara and Murakami, 2008; Ishihara et al., 2011a; Zhang et al., 1998), 9000 tons in the Japanese Islands (Ishihara et al., 2006), and more than 12,000 tons in Bolivia (Ishihara et al., 2011b, Table 1). These resource evaluations for indium also reported high In contents in zinc concentrates and composite samples from major tin polymetallic deposits, especially the Huari Huari deposit (Alfantazi and Moskalyk, 2003), indicating high 1000In/Zn ratios in zinc concentrates, zinc ores, and composite samples (Table 2).

The reported chemical analyses give the following concentrations of In and 1000In/Zn ratio, respectively; from Japan (Ishihara et al., 2006): 1030 ppm and 2.1 (for zinc concentrate from Toyoha), 49 ppm and 3.1 (for an average-grade In-bearing ore from Ashio),

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Fig. 1. Distribution of In-bearing ore deposits in the world (modified from Schwarz-Schampera and Herzig, 2002). Surrounded areas show the enlarged map for locations of In-bearing deposits, including the investigated deposits in China (a), Japan (b) and Bolivia (c).

and 248 ppm and 0.5 (for a sphalerite rich ore from Akenobe); from Bolivia (Ishihara et al., 2011b): 3080 ppm and 11.3 (for composite samples from Huari Huari), 292 ppm and 7.3 (for composite samples from Potosi), 584 ppm and 1.7 (for zinc concentrate from Bolivar), 499 ppm and 1.2 (for composite samples from Porco); from China (Ishihara et al., 2011a): 172 ppm and 3.3 (for composite samples from Dulong) and 410 ppm and 2.8 (for composite samples from Dachang). The maximum 1000In/Zn ratios in a single ore sample are 22.19 for Potosi deposit, 11.28 for Huari Huari deposit, and 7.42 for Bolivar deposit (Ishihara et al., 2011b).

Indium-bearing minerals have been reported from localities worldwide by many researchers (Ishihara et al., 2011b; Murao and Furuno, 1991; Ohta, 1989; Seifert and Sandmann, 2006; Shimizu et al., 1986; Sinclair et al., 2006). Indium-bearing sphalerite also occur in many Bolivian tin polymetallic deposits (Ishihara et al., 2011b; Sugaki et al., 2008), and sphalerite is the most important carrier of indium in the major tin polymetallic deposits. Representative reports of indium concentration in sphalerite indicate up to 8.86 wt.% for the Toyoha deposit (Ohta, 1989) and 1.83 wt.% for the Ikuno deposit, Japan (Ishihara et al., 2006); 6.90 wt.% for the Mount Pleasant deposit, Canada (Sinclair et al., 2006); 2.85 wt.% for the Freiberg district, Germany (Seifert and Sandmann, 2006); 1.2 wt.% for the Potosi deposit, 2.0 wt.% for the San Vincente deposit, Bolivia (Sugaki et al., 1983; Sugaki et al., 2008); 2.57 wt.% for the Pingüino deposit, Argentina (Jovic et al., 2011); and 3.4 wt.% for Sarvlaxviken area, Finland (Cook et al., 2011a). Roquesite (CuInS₂) has been described in the Toyoha, Ikuno, Mount Pleasant, Freiberg, San Vicente and Pingüino deposits, as well as Sarvlaxviken area. Although roquesite would be expected in the Potosi and Huari

| Table 1 | | | |
|------------------|-------------|-----------------|----------|
| Indium ore grade | and tonnage | of the selected | deposits |

| Deposit | Country | Tonnage (Mt) | In (g/t) | In (t) |
|-----------------------|--------------|--------------------|------------------|-------------------|
| VMS | | | | |
| Kidd Creek | Canada | 135.0 ¹ | 50 ¹ | 6750 |
| Brunswick No.12 | Canada | 161.0 ¹ | 50 ¹ | 8050 |
| Heath Steele | Canada | 33.8 ¹ | 50 ¹ | 1690 |
| Neves-Corvo | Portugal | 261.5 ¹ | 18 ¹ | 4707 |
| Letneye | Russia | 10.0 ¹ | 1 ¹ | 10 |
| Komsomolskoye | Russia | 25.0 ¹ | 2 ¹ | 50 |
| Podolskoye | Russia | 80.8 ¹ | 6 ¹ | 485 |
| Sibaiskoye | Russia | 100.0 1 | 10 ¹ | 1000 |
| Gaiskoye | Russia | 300.0 ¹ | 24 ¹ | 7200 |
| Maranda J | South Africa | 2.7 ¹ | 50 ¹ | 135 |
| Tin polymetallic vein | | | | |
| Freiberg | Germany | 4.7 ¹ | 1 ¹ | 5 |
| Tosham | India | 1.0 ¹ | 2 ¹ | 2 |
| San Vicente | Bolivia | 20.0 ¹ | 1 ¹ | 20 |
| Bolivar | Bolivia | 7.3 ¹ | 150 | 1092 ³ |
| Colquiri | Bolivia | 17.7 ¹ | 37 | 484 ³ |
| Porco | Bolivia | 19.3 ¹ | 52 | 997 ³ |
| Huari Huari | Bolivia | 3.0 ¹ | 1867 | 5600 ³ |
| Potosi | Bolivia | 140.0 ¹ | 29 | 4030 ³ |
| Dulong | China | 28.0 ⁴ | 183 ⁴ | 5124 |
| Dachang | China | 75.0 ⁴ | 117 ⁴ | 8795 |
| Toyoha | Japan | 33.7 ² | 138 ² | 4651 |
| Ashio | Japan | 24.8 ² | 49 ^{2a} | 1240 |
| Akenobe | Japan | 17.5 ² | 50 ² | 875 |
| Ikuno | Japan | 17.1 ² | 64 ² | 1094 |
| Sn-W vein stockwork | | | | |
| Mount Pleasant | Canada | 19.8 ¹ | 45 ¹ | 897 ¹ |
| Baal Gammon | Australia | 3.0 ¹ | 50 ¹ | 150 ¹ |
| Cinovec | Czech | 50.0 ¹ | 1 ¹ | 50 ¹ |

1 = (Schwarz-Schampera and Herzig, 2002); 2 = (Ishihara et al., 2006); 3 = (Ishihara et al., 2011a); 4 = (Ishihara et al., 2011b).

^a Historical production of Cu used, instead of Zn.

Huari deposits on the basis of the high 1000In/Zn ratio in ores, it has not yet been found. It remains unclear why the sphalerite in this deposit is so strongly enriched in indium.

Sphalerite is a scavenger of wide variety of elements, such as Fe, Mn, Cd, Cu, Sn Ag Ga, as well as In (Cook et al., 2009; Ye et al., 2011). This paper examines the trace elements geochemistry of sphalerite and some other In-bearing minerals in selected tin-polymetallic deposits. We use femto-second laser-ablation inductively coupled mass spectros-copy (fsLA-ICPMS) instrumentation, supported by electron microprobe analysis. Our aim is to clarify relationships between the high 1000In/Zn ratio in ore and the In content of sphalerite, and discuss correlations between trace elements and the mode of occurrence in these ore deposits.

2. Geological setting for major indium-bearing tin-polymetallic ore deposits

In this study, we selected major In-bearing tin-polymetallic ore deposits: Toyoha, Ashio and Akenobe in Japan; Huari Huari, Potosi, Bolivar and Porco in Bolivia; Dulong and Dachang in China. Geological features of the selected deposits are outlined below (Table 2).

2.1. Japan

The tin-polymetallic deposits in Japan occur as mainly vein and partly as replacement types; the latter is typified by the Kajika orebody within the Ashio deposit. The Toyoha and Ashio deposits are hosted in Miocene and younger volcanic rocks, while the Akenobe vein deposits occur in Paleozoic meta-sedimentary rocks. The late Cretaceous and Miocene intrusive rocks of Japan are categorized into the magnetite-series and ilmenite-series (Ishihara, 1977). Despite this, the volcanic rocks hosting the studied polymetallic deposits cannot be readily classified into either series owing to the intense hydrothermal alteration, even if the mineralized areas around Toyoha and Ashio are located within magnetite-series terrains, and the Akenobe deposits within the ilmenite-series terrains (Ishihara et al., 2006).

2.2. Bolivia

Major indium-bearing tin-polymetallic deposits in Bolivia are mostly vein and fissure-filling types hosted in Lower Paleozoic sedimentary rocks, and Miocene rhyolitic or dacitic tuff and tuff breccia, and subvolcanic intrusions (Sugaki and Kitakaze, 1988). Sugaki et al. (1988b) found that most of the Bolivian granitoids belong to the ilmenite-series; this classification has not been done in the individual ore deposit areas. Sillitoe et al. (1975) proposed a porphyry-type tin deposit, categorizing subvolcanic Sn-Ag mineralization. Grant et al. (1980) emphasized that Bolivian tin-polymetallic deposits are associated with high-level stocks and eruptive complexes based on proximity to the intrusive activities. Even though volcanic superstructure at Potosi contrasts with the collapsed caldera setting of Porco, both deposits were included within the so-called "volcanic-intrusive complexes" group by Grant et al. (1980); the maximum depth of ore deposition was estimated to range from 1 to 2 km according to the microthermometry. The tin-polymetallic deposits have mineralization ages of 20.5 to 12.0 Ma (Cunningham et al., 1994; Sugaki et al., 2003; Table 2). These ages lie within the range of the Tertiary (45.5–12.0 Ma) felsic intrusions (Sugaki et al., 1981), which are mostly composed of granodiorite to granitic rocks of I-type but ilmenite-series suites (Ishihara et al., 2011b; Sugaki et al., 1988b).

2.3. China

The Dachang ore deposits (indium reserves >8000 tons; (Zhang et al., 1998)), including the Changpo-Tongkeng Sn–Pb–Zn orebody (>4000 tons), and the Sn–Zn deposit at Dulong (>5000 tons; Ishihara et al., 2011a) are the two main indium-tin resources in China (Zhang et al., 1998). Both deposits are interpreted to have formed in a plutonic environment, based on the observation that the massive lenses occur in metamorphic and sedimentary rocks and result from hydro-thermal activity associated with Late Yanshanian S-type granites. This is evidenced by Rb–Sr isotopic dating for the Dulong deposit (Liu et al., 1999).

The Dachang ore deposits occur in Devonian to Permian sedimentary sequences of impure carbonates with intercalated sandstone, shale and chert. The Yanshanian granitic rocks occur widely below the Changpo-Tongkeng and Longxianggai orebodies, and are considered to be genetically related (Ishihara et al., 2011a; Jiang et al., 1999; Peng et al., 1997). The deposits consist of three types, based on the mode of occurrence of the ore minerals (Peng et al., 1999). These are: (1) veins, including veinlets and networks (e.g., the upper part of the Changpo-Tongkeng, Longtaoshan and Dafulou orebodies); (2) stratiform ores (e.g., Nos. 91 and 92 orebodies of the Changpo-Tongkeng deposit (Ishihara et al., 2011a)); and (3) skarn ores (e.g., Lamo). Average ore grades are 1% Sn, 2% Cu, 3.5% Zn, 5% Pb, 4% Sb and 100 ppm Ag. Total ore reserves discovered in the Dachang orefield are about 80 Mt, of which 70% occurs in the largest orebody (Changpo-Tongkeng). The Changpo-Tongkeng and Longtaoshan (or No. 100) orebodies are the most important sources of indium, which is carried within sphalerite and Pb-Sb sulfosalts (Murao et al., 1991; Zhang and Li, 1982; Zhang et al., 1998 and references therein).

The depth at which mineralization was formed in some of these deposits has been estimated based on fluid inclusion evidence or geological reconstruction (Table 2). Bolivian deposits such as Potosi (e.g., Sillitoe et al., 1975) and the Toyoha deposit in Japan (e.g., Shimizu and Morishita, 2012) are thought to have formed at shallower level compared with the other studied deposits, including those in China (e.g., Pasava et al., 2003). The shallower and deeper deposits can be differentiated in terms of the time-space relationships with volcanic rocks in

| Table 2 | 2 |
|---------|---|
|---------|---|

Geological features of selected polymetallic ore deposits.

| Country Deposit | | Concen represe sample | Concentration of representative sample | | Concentration of representative sample | | Concentration of representative sample | | Age | Mode of occurrence | Ore mineral assemblage | Related igneous rock | Host rock | Formation temperature range (°C) | Salinity wt.% NaCl | Estimated depth (km) | Reference |
|-----------------|--|-----------------------------|--|-----------|---|---|--|---|--|-----------------------|---------------------------|----------------------------------|---|--|--------------------------|----------------------------|-----------|
| | | In (g/t) | Zn (%) | 1000In/Zn | | | | | | | equiv | | | | | | |
| Japan | Toyoha | 1030 ¹ | 48.3 | 2.1 | 2.9–3.2 Ma ² 12.8 Ma ³ | Vein | Early stage: Py, Sph, Gl, Mgt Later stage: Sph, Po, Py, Marc, Stn ³ | Latent granitic rocks? ⁴ | Miocene andesite and basaltic andesite | 150-400 ⁵ | 0-4.2 ⁵ | 1-2 ² | Ishihara et al. (2006), Shimizu and Morishita (2012), Ishihara et al. (2010), Ohta (1989), Yaiima and Ohta (1979) | | | | |
| | Ashio (Kajika) | 49 ¹ | 1.6 | 3.1 | Miocene? | Vein and partly replacement ⁶ | Cp, Py, Sph, Gl, Po | Latent granitic rocks? ⁶ | Triassic rhyolite and acidic volcanic complex with minor Jurassic sediments | 250-350 ⁷ | 0-9 ⁷ | n.a. | Ishihara et al. (2006), Nakamura (1970), Imai et al. (1975) | | | | |
| Dellada | Akenobe (Chiemon vein: Early stage vein) | 248 ¹ | 54.7 | 0.5 | 72.8 Ma post ore rhyolite dyke ⁸ | Vein (xenothermal) | Early stage: Cp, Sph, Mgt, Apy Later stage: Cas, Wolf, Sch ⁸ | Late Cretaceous felsic igneous rocks or latent granitic rocks? | Paleozoic meta- sedimentary-igneous rocks | 155–355 ⁷ | n.a. | n.a. | Ishihara et al. (2006), Imai et al. (1975), Ishihara and Shibata (1972), Saigusa (1958) | | | | |
| Bolivia | Potosi | 292 ¹⁰ | 7.3 | 4.0 | 13 Ma | Vein | Early stage: Cas, Py, Wolf, Later stage: Sph, Stn, Tet, Jam | Volcanic intrusive complex: Miocene dacite with felsic tuffbreccia ¹¹ | Ordvician slate and Mesozoic sandstone | 243-315 ¹² | 4.7-13.5- | 1.5–3.0 ¹³ | Ishihara et al. (2011b), Turneaure (1960), Sugaki et al. (1988a), Sillitoe et al. (1975) | | | | |
| | Huari Huari | 3080 ¹⁰ | 27.3 | 11.3 | 20 Ma | Vein | Sph, Py, Gl, Marc, Iam, Cas, Pyr | Miocene dacite? ¹⁴ | Ordvician slate and sandstone | 42115 | n.a. | n.a. | Ishihara et al. (2011b), Sugaki et al. (1983, 1990) | | | | |
| | Bolivar | 584 ¹⁰ | 34.4 | 1.7 | 3.9 Ma ¹⁶ | Vein, fissure-filling | Sph, Py, Jam, Cas ¹⁷ | Quartz porphyry | Silurian shale and siliceous sandstone | 198-327 ¹⁴ | Less than 10 | n.a. | Ishihara et al. (2011b), Sugaki et al. (1981, 1983, 2003) | | | | |
| China | Porco | 499 ¹⁰ | 40.7 | 1.2 | 12 Ma | Vein | Cas, Sph, Gl, Py | Felsic stocks | Ordvician phyllite | 219-235 ¹⁸ | 8–10 | n.a. | Ishihara et al. (2011b), Cunningham et al. (1994) | | | | |
| Clillia | Dulong | 172 ¹⁹ | 5.2 ¹⁹ | 3.3 | Late Yanshanian (ca. 70–75 Ma) ²⁰ | Vein and partly stratiform andskarn ²¹ | Mgt, Cas, Sph, Po ²⁰ | Yanshanian S-type granite | Cambrian chlorite- muscovite schist and marble | n.a. | n.a. | n.a. | Ishihara et al. (2011a), Liu et al. (1999), Peng et al. (1997) | | | | |
| | Dachang(Changpo- Tongkeng orebody) | 410 ¹⁹ | 14.4 ¹⁹ | 2.8 | 91 Ma | Massive lens with minute layering and veining ¹⁹ | Py, Po, Sph, Apy, Cas ²² | Peraluminous granite (Yanshanian) | Devonian calcareous blackshale | 360-390 ²³ | 1.8–14.8 | 5–7.5 (about 6) ²³ | Ishihara et al. (2011a), Zhang et al. (1998), Pasaya et al. (2003) | | | | |

1 = Sample THZn for Toyoha, AS20 for Ashio, AK2306 for Akenobe in (Ishihara et al., 2006); 2 = (Shimizu and Morishita, 2012); 3 = (Ishihara et al., 2010); 4 = (Ohta, 1989); 5 = (Yajima and Ohta, 1979); 6 = (Nakamura, 1970); 7 = (Imai et al., 1975); 8 = (Ishihara and Shibata, 1972); 9 = (Saigusa, 1958); 10 = Composite samples of PTC2 for Potosi and HUC for Huari Huari, Zn concentrate of PORZn for Porco and BOLZn for Bolivar in (Ishihara et al., 2011b); 11 = (Turneaure, 1960); 12 = (Sugaki et al., 1988); 13 = (Sillitoe et al., 1975); 14 = (Sugaki et al., 1983); 15 = Sulfur isotopic temperature in (Sugaki et al., 1990); 16 = (Sugaki et al., 2003); 17 = (Sugaki et al., 1981); 18 = (Cunningham et al., 1994); 19 = Average of zinc ores, 11 samples for Dulong, 4 samples for Dachang in (Ishihara et al., 2011a); 20 = (Liu et al., 1999); 21 = (Peng et al., 1997); 22 = (Zhang et al., 1998); 23 = (Pasava et al., 2003). n.a. = not available. Sph = sphalerite; Cp = chalcopyrite; Py = pyrite; Gl = galena; Mgt = magnetite; Po = pyrrhotite; Stn = stannite; Marc = marcasite; Cas = cassiterite; Wolf = wolframite; Sch = Scheelite; Apy = arsenopyrite; Tet = tetrahedrite; Jam = Jamesonite; Pyr = pyrargyrite.

and around the deposits, and the genetic association with a plutonic environment, respectively. More complete reviews of the geology and mineralization of the Japanese, Bolivian and Chinese tin-polymetallic deposits can be found in the references given in Table 2.

3. Samples and analytical methodology

3.1. Samples

We used a suite of relatively high-In samples which are the same specimens as previously reported in (Ishihara et al. (2006, 2011a, b). Table 3). Microscopic observation of the selected ores from the tinpolymetallic deposit are summarized as follows (Fig. 2).

3.1.1. Toyoha deposit

Sample THZn of Ishihara et al. (2006) was taken from zinc concentrates produced in January 2006, three months before production ceased at Toyoha. Under the microscope, the concentrate is mostly composed of black sphalerite, several tens of microns in size, together with trace amounts of pyrrhotite, pyrite and chalcopyrite. Although indium is commonly enriched in sphalerite, the sphalerite grains in the concentrates are too small to recognize a whole series of thin growth zones reflecting the oscillatory zonation of indium which occurs within single sphalerite grains (Ohta, 1989; Shimizu and Morishita, 2012).

3.1.2. Ashio deposit

Sample ASK3 of Ishihara et al. (2006) is a massive black sphalerite ore taken from 8 L of the so-called Zinc Kajika orebody which replaces Jurassic chert (Asano, 1952). The sample contains black sphalerite, euhedral quartz and minor pyrrhotite. The black sphalerite generally shows no transparency, and coexists with the euhedral quartz (Fig. 2e). The latter contains abundant two-phase fluid inclusions ranging in size from 20 to 30 µm. Minor amounts of stannite are observed within the black sphalerite, occasionally occurring along the sphalerite crystal growth zone. A less common, reddish, translucent sphalerite occurs at the contact between black sphalerite and euhedral quartz.

3.1.3. Akenobe deposit

Sample AK2307 of Ishihara et al. (2006) is a massive black sphalerite ore taken from - 13L of the Chiemon No. 4 vein system. This deposit is characterized by high-temperature Sn-W-bearing quartz

Table 3

Selected samples of polymetallic ore deposits.

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veins which occur later than low-temperature guartz veins carrying base metal (Saigusa, 1958). The sample conforms to a Cu-Zn vein of Ishihara et al. (1981), and corresponds to the earlier generation of base metal quartz veins. The sample mainly contains sphalerite with minor chalcopyrite, stannite and galena. The latter minor minerals commonly occur along sphalerite grain boundaries. The sphalerite is crowded with minute inclusions of chalcopyrite, and has no chemical and oscillatory zoning (Fig. 2f). Sphalerite, however, contains vermiculated poikilitic fragments showing a distinct sub-transparency and pale purple in color, contrasting with the otherwise homogeneous appearance of the black sphalerite in reflected light.

3.1.4. Potosi deposit

We investigated three samples from the Potosi deposit. These have 1000In/Zn ratios ranging from 1.4 to 22.19 and were taken from the Mauricio Vein which is peripheral to the central veining system at Potosi (Ishihara et al., 2011b). Sample 98110509 is a massive black late-stage sphalerite ore characterized by an assemblage of oscillatory-zoned sphalerite with stannite, tetrahedrite and Ag-minerals (Turneaure, 1960). Oscillatory-zoned sphalerite in this sample is composed of two apparent zones dividing into translucent and black opaque zones (Fig. 2a). The latter zone exhibits continuous thin film, being equivalent to one of the growth zones of oscillatory-zoned sphalerite (Fig. 2a). Samples 98110508A and -B are tuff-hosted vein materials, and are representative of the typical telescoping of ore minerals described by Sugaki et al. (1983) by which high-temperature cassiterite occurs together with low-temperature sphalerite and Sb-bearing minerals, such as polybasite [(Ag,Cu)₁₆Sb₂S₁₁], tetrahedrite [(Cu,Fe)₁₂ Sb₄S₁₃], jamesonite (Pb₄FeSb₆S₁₄), pyrargyrite (Ag₃SbS₃) and miargyrite (AgSbS₂). Sphalerite intermingled with cassiterite generally occurs as aggregates of fine-grained black sphalerite with no optical oscillatory zoning.

3.1.5. Huari Huari deposit

Sample HUC of Ishihara et al. (2011b) is a composite of massive black sphalerite ores. The sample is composed of dominant black opaque sphalerite with small amounts of pyrite, galena, jamesonite, boulangerite, cassiterite, pyrargyrite and miargyrite. Under the microscope, the sphalerite displays some oscillatory zoning, with alternation of weakly-translucent reddish zones with darker opaque zones (Fig. 2b). These oscillatory-zoned grains of sphalerite are >2 mm in size and are locally rimmed by aggregates of fine-grained cassiterite.

| Country | Deposit | Sample ¹ | Concentratio | on of sample ¹ | Ore mineral assemblage | |
|---------|------------------------------------|---------------------|--------------|---------------------------|------------------------|-----------------------------|
| | | | In (g/t) | Zn (%) | 1000In/Zn | |
| Japan | | | | | | |
| • | Toyoha | THZn | 1030 | 49.0 | 2.1 | Sph >> Po, Py, Cp |
| | Ashio (Kajika) | ASK3 | 698 | 46.5 | 1.5 | Sph and Qz>>Cp |
| | Akenobe (Chiemon vein) | AK2307 | 248 | 54.7 | 0.5 | Sph>Cp, Stn |
| Bolivia | | | | | | |
| | Potosi | 98110508A | 260 | 1.2 | 21.49 | Cas, Tet, Jam, Pyr, Mir>Sph |
| | | 98110508B | 233 | 1.1 | 22.19 | Cas, Tet, Jam, Pyr>Sph |
| | | 98110509 | 292 | 20.6 | 1.4 | Sph>>Cas, Tet, Jam |
| | Huari Huari | HUC | 3080 | 27.3 | 11.3 | Sph>Pyr, Jam, Mir |
| | Bolivar | B1905 | 2730 | 36.9 | 7.4 | Sph, Py, Jam, Cas |
| | Porco | 98110401 | 172 | 53.8 | 0.32 | Sph>>Py |
| China | | | | | | |
| | Dulong | 1122A2 | 344 | 15.6 | 2.2 | Mgt, Cas, Sph, Po |
| | Dachang (Changpo-Tongkeng orebody) | 8111907 | 1370 | 41.3 | 3.3 | Sph, Py, Po, Apy, Cas |
| | | 8111908 | 126 | 3.5 | 3.6 | Py, Po, Sph |

1 = Samples for Toyoha, Ashio and Akenobe taken from Ishihara et al. (2006); samples for Potosi, Huari Huari, Porco and Bolivar taken from Ishihara et al. (2011b); samples for Dulong and Dachang taken from Ishihara et al. (2011a). Sph=sphalerite; Cp=chalcopyrite; Py=pyrite; Po=pyrrhotite; Stn=stannite; Cas=cassiterite; Tet=tetrahedrite; Jam = jamesonite; Pyr = pyrargyrite; Mir = miargyrite; Qz = quartz.



Fig. 2. Microscopic photographs of occurrence of sphalerite (Sph) of the selected samples. The same sample indicates as the same alphabetical character with a set of upper open nicol and bottom reflected right photographs for each sample; (a) = 98110509 from Potosi deposit; oscillatory-zoned sphalerite composed of two apparent zones dividing into translucent and black opaque zones, (b) = HUC from Huari Huari deposit; oscillatory-zoned sphalerite exhibiting alternation of weak translucent reddish zones and opaque sphalerite zones, (c) = B1905 from Bolivar deposit; sphalerite zoned from opaque sphalerite of core through translucent mantle to opaque sphalerite rim, (d) = 98110401 from Porco deposit; significant oscillatory-zoned sphalerite, (e) = ASK3 from Ashio deposit; reddish translucent sphalerite coexisting with the euhedral quartz (Qz), (f) = AK2307 from Akenobe deposit; sphalerite crowded with minute chalcopyrite containing vermiculated poikilitic fragments showing sub-transparency of pale purple under the open nicol, (g) = 1122A2 from Dulong deposit; sphalerite showing a brownish transparency with sporadically opaque, dusty parts which contain chalcopyrite grains, (h) = 8111907 from Dachang deposit; sphalerite showing with reddish translucent parts including many chalcopyrite blebs, and coexisting with actinolite (Act) and quartz (Qz). Scale bars = 0.2 mm.

3.1.6. Bolivar deposit

Sample B1905 of Ishihara et al. (2011b) is a massive black sphalerite ore, composed of medium-grained (<1 mm) euhedral sphalerite and quartz which occupies sphalerite grain boundaries. The sphalerite generally displays an optically-visible zonation from opaque sphalerite in the grain core through translucent mantle to an opaque sphalerite rim (Fig. 2c). The opaque sphalerite core is not observed partly. According to Sugaki et al. (1981), other ore minerals present are pyrite, jamesonite and stannite, which occur together with microscopic amounts of cassiterite and chalcopyrite, and a late-stage marcasite.

3.1.7. Porco deposit

Sample 98110401 of Ishihara et al. (2011b) is a coarse-grained massive black sphalerite ore in which the sphalerite shows significant oscillatory zoning in terms of alternation of translucent orange-colored zones and darker zones (Fig. 2d).

3.1.8. Dulong deposit

Sample 1122A2 is taken from at 1170 mL of the main open pit. The ore occurs as massive lens dominating black sphalerite with minute layering and veining of magnetite and chalcopyrite. Major ore constituents are composed of magnetite, cassiterite, sphalerite, pyrrhotite,

actinolite, chlorite, sericite, quartz and calcite. Magnetite is locally abundant in the ore. Sphalerite commonly shows a brownish in color with reddish translucent parts, and includes many chalcopyrite grains and blebs (Fig. 2g). Indium is contained homogeneously in the sphalerite (Murakami and Ishihara, 2008).

3.1.9. Dachang deposits

Sample 811907 is taken from the Changpo-Tongkeng orebody, No. 92, at 445 mL. The ore exhibits a stratiform structure and is located mostly along bedding planes in the sedimentary rocks. Sphalerite is the main constituent, and is associated with chlorite, muscovite, quartz and calcite. Sphalerite commonly shows a reddish transparency with sporadically opaque dusty parts, and includes many chalcopyrite blebs (Fig. 2h). The chalcopyrite blebs are relatively pronounced and coarse-grained in the opaque dusty parts in sphalerite.

3.2. Analytical methodology

This study employed a combination of two microanalytical techniques: femto-second laser-ablation inductively coupled mass spectroscopy (fsLA-ICPMS) and electron probe microanalysis (EPMA). Minimum detection limits for each element using each method are given in Appendix A.

3.2.1. EPMA

A JEOL JXA-8900R electron probe microanalyzer (Geological Survey of Japan, AIST) was employed to obtain back-scattered electron images of In-bearing minerals and to constrain their mineral compositions. Chemical heterogeneity was also investigated by mapping before the quantitative analysis using EPMA and fsLA-ICPMS. Accelerating voltage, sample current and spot size were 20 kV, 15 nA and 4 µm, respectively, for quantitative analyses, and 15 kV, 50 nA and from 1 to 0.2 µm, respectively, for compositional mapping. Counting times of 20 and 10 s were used for element detection and background, respectively. ZAF-atomic number (Z), absorption (A), and fluorescence (F) method was used for matrix corrections. The following characteristic X-ray lines were measured for all points: SKa, CuKa, AsLa, ZnKa, AgLa, CdLa, MnKa, InLa, FeKa, BiLa, SbLa and SnLa. Calibration standards were pure metals (In, Ag, Cu, Mn Bi, Sb and Sn) and synthetic metal compounds (InAs for As, CdS for Cd) and pyrite for Fe and sphalerite for Zn and S.

3.2.2. fsLA-ICPMS analysis

Analysis took place using a Cyber Laser System IFRIT femto-second Laser ablation system (fsLA-ICPMS) coupled to an Agilent 7500cx inductively-coupled mass spectrometer. The laser ablation system (LA) is equipped with a 220 femto-second Ti-Sapphire laser of wavelength 780 nm with a repetition rate of 10 Hz, beam spot size of 15–25 μ m (diameter) and an adjustable laser power of 10–50% (100% corresponds to about 20 J/cm²) to produce controlled sampling depth below 100 μ m. The ablation cell is an in-house-built small-volume (3 cm³) ablation cell containing no organic materials, except for an O-ring that is hidden in a groove below the top glass cover. The sample is prepared as a doubly-polished thin section (about 150 μ m in thickness) and placed in the ablation cell. Each spot was analyzed by EPMA before measurement by fsLA-ICPMS. Due to the large beam laser spot size, it is difficult to avoid the influence of sub-micron size inclusions in a single analysis.

Ablation was performed with a pure helium flow (0.8 l/min). The helium gas carrying the ablated aerosol was mixed with Ar (1.0 l/min) immediately after the ablation cell and directly introduced to the torch in the mass spectrometer. The mass spectrometer was optimized for the detection of mid-mass isotopes such as indium with respect to dry gas backgrounds and sensitivities, while maintaining multi element capability for the simultaneous measurement of metals of interest. A set of isotopes (55Mn, 57Fe, 63Cu, 66Zn, 69Ga, 75As, 107Ag, 111Cd, 115In, 118Sn, ¹²¹Sb, ²⁰⁸Pb, ²⁰⁹Bi) was measured with dwell times of 0.02 s for each element. The attempt to obtain quantitative data for As was unsuccessful because the signal could not be detected above a few tens of $\mu g/g$ in all samples, suggesting As concentrations are below the minimum detection limit of 27 µg/g across the dataset. The analysis time for individual sample was 100 s-20 s background measurement, 15 s measurement (laser on), and 65 s for sweep the chamber (laser off). Gas blanks on mass 32 range about 4000 count per second (cps) (from ¹⁶O¹⁶O and ³²S in ambient air, He carrier and Ar plasma gas; Guillong et al., 2008), other isotopes are less than 10 count per second (cps). For Cu signal, we measured ⁶³Cu in preference to ⁶⁵Cu, because no significant interference from ArNa (mass abundance 63) was observed during analysis. Absolute concentrations of elements are calculated by internal standardization against Zn for sphalerite and Ag for miargyrite and pyrargyrite, and Pb for jamesonite, based on EPMA data. The NIST SRM 610 (NIST610) glass was used for calibration and as a standard reference material for each element for the laser-ablation ICP-MS. Some previous works have suggested that a matrix-matched, sulfide standard would be optimal for calibration and quantitative analysis (e.g., Danyushevsky et al., 2003, 2011; Ding et al., 2011). Despite this and discussion of the importance of the standard matrix on calibration and analysis, femto-second laser has the advantage of being able to detect higher transient ICPMS signals for metal and glass samples than a nano-second laser (Glaus et al., 2010 and references therein). Based on the comparison between the EPMA analysis and LA-ICPMS results, no significant bias is identified in this study (Fig. 3), suggesting that matrix-matching is not critical for external normalization of fsLA-ICPMS quantitative measurements. We also monitored the values of the NIST610 reference material during analytical runs (Appendix B). Compared with values for the NIST610 glass which has previously been quantified by various methods (e.g., Jochum et al., 2011), most of our results show a good correlation with the certified or reported values within an uncertain range of 10 μ g/g, except for Sn, Sb and Bi, which are within 20 μ g/g.

In most of the data, each of the elements measured with EPMA is slightly higher than those measured by fsLA-ICPMS. This may arise from an underestimation of Zn concentration in the EPMA analyses owing to a possible difference in the peak wavelength between the standard for Zn and the analyzed sphalerite (e.g., Reed, 2005). Elements present in greater concentration in sphalerite such as Fe, Mn and Cd determined by both EPMA and fsLA-ICPMS fall on or close to the 1:1 line, confirming the accuracy and robustness of the two techniques (Fig. 3). Indium. Cu and Sn also show good to moderate correlations. In the case of Cu and Sn, however, the elements deviate by different amounts. This probably results from the small number of sub-micron inclusions of phases such as stannite and chalcopyrite which are randomly distributed in the sphalerite. Relatively higher concentrations of Cu and Sn, either in the EPMA or fsLA-ICPMS data, may appear in cases either when sub-micron inclusions are relatively concentrated on the sample surface, or when inclusions are present at depth. Nevertheless Fe contents determined by both EPMA and fsLA-ICPMS indicate relatively good correlation as compared with Cu and Sn, the deviation of Fe causing by the sub-micron inclusions such as stannite and chalcopyrite could merge into sphalerite which normally indicates one-digit higher Fe concentration ranging from 1 to 10 wt.% than Cu and Sn (0.1 to 1 wt.%). Another point of view, Glaus et al. (2010) reported that elemental separation within the particle fractions was produced with fs-LA of brass (Cu/ Zn). They interpreted that the amount of Cu transported into the ICPMS decreased due to the preferred formation of large particles of Cu, resulting in greater amounts of debris with increasing crater depth. Furthermore, the ICPMS signal for Sn correlates with the Cu signal, influencing additional fractionation of the analytical results for Cu and Sn. Although there are several hypothetical explanations, the observed element separation in Cu and Sn is likely to remain an unresolved question.

fsLA-ICP-MS is deemed as a suitable method for analyzing major and trace elements in sphalerite. This is supported by the accuracy on measurements of NIST 610 and the generally good agreement in analytical results between the fsLA-ICPMS and the EPMA.

4. Results

4.1. Quantitative analysis via EPMA with compositional mapping

Table 4 summarizes the quantitative EPMA analyses of sphalerite in the selected samples. Indium occurs mostly in less translucent black sphalerite. Sphalerites from the deposits in Japan and Bolivia readily display oscillatory zoning partly comprising zones with high concentrations of In (>1 wt.%) coexisting with Cu–Sn rich minerals such as stannite and petrukite in a single crystal (e.g., Ishihara et al., 2011b). Oscillatory-zoned black sphalerites from Bolivian deposits show chemical heterogeneity. Generally, the Fe content, which is higher in the black sphalerite, positively correlates with concentrations of Sn, Cu and In; these elements are compensated by a decrease in the Zn content. The similar positive correlation among In-Cu–Sn and the presence of high-In growth zones are also observed in sphalerites from Japanese deposits (e.g., Ohta, 1989; Shimizu and Morishita, 2012), while a chemical heterogeneity is less apparent in the Ashio and Akenobe deposits.

Among the selected deposits, elevated In, Cu and Sn contents are more obvious in sphalerite from the Potosi and Huari Huari deposits than the others, supporting the high 1000In/Zn values of the bulk



Fig. 3. Comparison between EPMA and fsLA-ICPMS analyses of Fe, Mn, Cd, In, Sn and Cu in sphalerite from the selected deposits. Some deposits are not shown owing to the lower values than limit of detection of EPMA analysis.

ore in these deposits (Fig. 4; Table 5). The elevated In-Cu-Sn parts in our studied samples from Potosi and Huari Huari deposits are subject to occur as continuous thin film being equivalent to opaque black sphalerite zone (Fig. 4). In the Potosi deposit, fine-grained black sphalerite associated with cassiterite and Ag-Sb-bearing minerals includes parts that are higher in In (Fig. 4a2), compared with oscillatory-zoned sphalerite which contains less than 0.5 wt.% In (Fig. 4b2; Tables 4 and 5). The fine-grained black sphalerite records a uniform ratio of atomic proportion of Cu to In as almost 1:1 (sample 98110508B in Tables 4 and 5), whereas that of Cu to Sn in oscillatoryzoned sphalerite is about 2:1 (sample 98110509 in Tables 4 and 5). With respect to sample 98110509, the black sphalerite zone of the oscillatory-zoned sphalerite from the Potosi deposit has higher Fe, Cu, Sn and In and lower Cd contents relative to the translucent zone (Table 5). Silver-Sb-bearing minerals such as pyrargyrite and miargyrite from the Potosi deposit have simple chemical compositions corresponding to their ideal stoichiometries (Table 6). In the Huari Huari deposit, oscillatory-zoned sphalerite is normally coarsegrained and occasionally forms crystals up to 2 mm in diameter. The oscillatory-zoned sphalerites show rhythmic banding, containing high-In zones that are enriched also in Cu, and partly also in Sn (Fig. 4c2, c3 and c4). The high-In zones are in agreement with the locations of black opaque sphalerite zones enriched in Fe, while weak translucent reddish zones exhibit low In, Cu and Sn contents. In particular, very fine-grained minerals, with triangular cross section occur in the high-In zone where is close to core of the oscillatoryzoned sphalerite (Fig. 5). Based on the range of In concentration (up to 18 wt.%; Table 5), this mineral chemically resembles the unnamed Zn–In mineral which was reported from the Toyoha deposit by (Ohta, 1989), and also from the Mount Pleasant deposit, Canada (Sinclair et al., 2006). Antimony-bearing minerals such as miargyrite and jamesonite from the Huari Huari deposit, partly coexisting with oscillatory-zoned sphalerite, have almost theoretical chemical composition with minor amount of Fe (Table 6).

On the basis of EPMA analysis, sphalerite from the Potosi and Huari Huari deposits are plotted in the ternary diagram in Fig. 6. Most fall within two compositional trends that follow the sphalerite (Sp)-roquesite (Rq) and sphalerite-stannite (St) tie-lines. For the Potosi deposit, oscillatory-zoned sphalerites plotted at the Zn-rich end of the Sp–St join, whereas the fine-grained ones plot either along the Sp–Rq tie-line, or in the middle of these two tie-lines. For the Huari Huari deposits, significant discrimination between the two tie-lines is observed; low-In sphalerite plots along the Sp–St tie-line, whereas the Zn–In mineral is consistent with the Sp–Rq tie-line (Fig. 6).

In contrast, sphalerites from the Chinese deposits are characterized by homogeneous compositions with respect to In (Fig. 7), and also show no correlation between Cu–Sn and In. The black, dusty portions show low Zn content due to slight increase in Cu for the Dulong deposit and Cu and Sn for the Dachang deposit, respectively (Fig. 7), while In content is relatively constant (Table 4).

4.2. fsLA-ICPMS analysis

For analysis by means of fsLA-ICPMS, we mainly investigated low-In sphalerites possessing a typical range of trace elements as reported in Cook et al. (2009). In doing so, we avoided measurement of extremely high In parts of black sphalerite from the Potosi and Huari Huari deposits (Figs. 4 and 5; Table 5). The fsLA-ICPMS dataset is summarized in Tables 7 and 8 and includes mean values with

| Fabl | e | 4 | |
|------|---|---|--|
| | | | |

Summary of EPMA analysis for sphalerites from the selected deposits.

| Deposit | Sample | | Cu | Ag | Fe | Zn | Mn | Cd | Sn | In | S | Total |
|--------------|--------------------|---------------------|-------|------|-------|----------------|------|------|------|-------|-------|--------|
| | | LOD (wt.%) | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | |
| Toyoha | TYHZn | AV. (22) | 0.24 | 0.00 | 2.87 | 63.57 | 0.02 | 0.39 | 0.23 | 0.00 | 33.51 | 100.84 |
| | | S.D. | 0.32 | 0.00 | 1.30 | 1.55 | 0.02 | 0.26 | 0.29 | 0.00 | 0.34 | 0.68 |
| | | MAX | 1.32 | 0.00 | 5.70 | 67.31 | 0.08 | 0.99 | 1.23 | 0.00 | 34.70 | 102.33 |
| | | MINI | 0.00 | 0.00 | 0.70 | 60.87 | 0.00 | 0.00 | 0.00 | 0.00 | 33.13 | 99.58 |
| Ashio | ASK3 | AV. (54) | 0.52 | 0.00 | 11.95 | 53.26 | 0.01 | 0.47 | 0.29 | 0.15 | 33.83 | 100.49 |
| | | S.D. | 0.47 | 0.00 | 0.62 | 1.02 | 0.02 | 0.09 | 0.40 | 0.20 | 0.25 | 0.54 |
| | | MAX | 2.57 | 0.01 | 13.26 | 55.69 | 0.06 | 0.69 | 2.09 | 0.77 | 34.32 | 101.79 |
| | | MINI | 0.05 | 0.00 | 10.61 | 50.85 | 0.00 | 0.30 | 0.00 | 0.00 | 33.15 | 99.02 |
| Akenobe | AK2307 | AV. (27) | 0.05 | 0.00 | 0.32 | 66.46 | 0.00 | 0.49 | 0.01 | 0.01 | 33.09 | 100.43 |
| | | S.D. | 0.07 | 0.00 | 0.05 | 0.30 | 0.00 | 0.03 | 0.01 | 0.01 | 0.25 | 0.40 |
| | | MAX | 0.26 | 0.00 | 0.42 | 66.97 | 0.00 | 0.55 | 0.04 | 0.03 | 33.46 | 100.97 |
| | | MINI | 0.00 | 0.00 | 0.24 | 65.76 | 0.00 | 0.43 | 0.00 | 0.00 | 32.51 | 99.38 |
| Potosi | 98110508A | AV. (75) | 2.71 | 0.12 | 3.69 | 55.85 | 0.01 | 0.12 | 0.45 | 3.78 | 32.96 | 99.71 |
| | (Fine-grained) | S.D. | 1.61 | 0.17 | 0.33 | 3.79 | 0.01 | 0.04 | 0.75 | 2.37 | 0.40 | 1.04 |
| | | MAX | 7.03 | 0.95 | 4.41 | 63.65 | 0.04 | 0.17 | 4.62 | 8.45 | 33.63 | 101.54 |
| | | MINI | 0.12 | 0.00 | 2.81 | 47.18 | 0.00 | 0.00 | 0.00 | 0.14 | 31.04 | 96.35 |
| Potosi | 98110508B | AV. (40) | 2.96 | 0.12 | 3.57 | 55.39 | 0.01 | 0.10 | 0.29 | 4.28 | 32.76 | 99.50 |
| | (Fine-grained) | S.D. | 1.98 | 0.14 | 0.32 | 5.06 | 0.01 | 0.04 | 0.39 | 2.87 | 0.69 | 1.52 |
| | | MAX | 6.57 | 0.70 | 4.08 | 64.05 | 0.06 | 0.16 | 1.63 | 9.59 | 34.50 | 101.// |
| D (1 | 00110500 | MINI | 0.13 | 0.00 | 2.67 | 47.06 | 0.00 | 0.00 | 0.00 | 0.09 | 31.68 | 95.24 |
| Potosi | 98110509 | AV. (49) | 1.18 | 0.00 | 2.26 | 60.39 | 0.00 | 0.20 | 1.01 | 0.02 | 32.70 | 97.77 |
| | (Oscillatory) | S.D. | 1.03 | 0.00 | 0.94 | 2.24 | 0.00 | 0.14 | 0.93 | 0.04 | 0.43 | 0.67 |
| | | MAX | 5.64 | 0.00 | 4.89 | 63.20 | 0.02 | 0.59 | 5.08 | 0.22 | 33.43 | 99.15 |
| Dotosi | 00110500 | IVIIINI AV. (22) | 0.04 | 0.00 | 1.13 | 51.54 60.20 | 0.00 | 0.05 | 1.46 | 0.00 | 30.99 | 95.52 |
| FULUSI | (Plack sphalorite) | AV. (23) | 1.08 | 0.00 | 2.20 | 2 41 | 0.00 | 0.20 | 1.40 | 0.05 | 0.42 | 97.69 |
| | (black sphalente) | S.D. MAY | 5.64 | 0.00 | 1.04 | 62 73 | 0.00 | 0.05 | 5.08 | 0.00 | 22/2 | 0.58 |
| | | MINI | 0.27 | 0.00 | 1 29 | 51 54 | 0.02 | 0.27 | 0.20 | 0.22 | 31.28 | 96.79 |
| Potosi | 98110509 | AV (26) | 0.73 | 0.00 | 1.23 | 61.63 | 0.00 | 0.00 | 0.20 | 0.00 | 32.63 | 97.67 |
| 101051 | (Translucent) | SD | 0.73 | 0.00 | 0.49 | 1.05 | 0.00 | 0.17 | 0.55 | 0.02 | 0.42 | 0.75 |
| | (manoracent) | MAX | 2.01 | 0.00 | 3 2 9 | 63 20 | 0.02 | 0.59 | 1 94 | 0.10 | 33.21 | 99.15 |
| | | MINI | 0.04 | 0.00 | 1.13 | 59.28 | 0.00 | 0.05 | 0.00 | 0.00 | 30.99 | 95.52 |
| Huari Huari | HUA | AV. (131) | 2.94 | 0.19 | 9.64 | 50.38 | 0.01 | 0.33 | 0.88 | 3.08 | 33.07 | 100.51 |
| | | S.D. | 3.28 | 0.30 | 1.98 | 9.48 | 0.01 | 0.07 | 1.74 | 5.57 | 0.71 | 0.67 |
| | | MAX | 10.49 | 1.05 | 12.92 | 61.64 | 0.05 | 0.54 | 7.89 | 18.22 | 33.94 | 101.82 |
| | | MINI | 0.00 | 0.00 | 4.54 | 26.80 | 0.00 | 0.00 | 0.00 | 0.00 | 31.07 | 98.74 |
| Bolivar | B1905 | AV. (46) | 0.33 | 0.00 | 7.34 | 57.16 | 0.00 | 0.78 | 0.07 | 0.19 | 33.39 | 99.28 |
| | | S.D. | 0.16 | 0.00 | 1.39 | 1.64 | 0.01 | 0.12 | 0.07 | 0.23 | 0.19 | 0.27 |
| | | MAX | 0.67 | 0.00 | 9.80 | 59.80 | 0.02 | 1.05 | 0.30 | 0.69 | 33.71 | 100.14 |
| | | MINI | 0.06 | 0.00 | 5.28 | 53.88 | 0.00 | 0.48 | 0.00 | 0.00 | 33.00 | 98.72 |
| Porco | 98110401 | AV. (20) | 0.12 | 0.00 | 8.18 | 56.36 | 0.05 | 0.17 | 0.12 | 0.03 | 33.45 | 98.51 |
| | | S.D. | 0.18 | 0.00 | 2.56 | 2.71 | 0.04 | 0.03 | 0.18 | 0.09 | 0.26 | 0.54 |
| | | MAX | 0.52 | 0.00 | 13.27 | 60.30 | 0.16 | 0.22 | 0.50 | 0.39 | 33.86 | 99.46 |
| | | MINI | 0.00 | 0.00 | 4.44 | 51.09 | 0.00 | 0.10 | 0.00 | 0.00 | 32.89 | 97.32 |
| Dulong | 1122A2 | AV. (35) | 0.26 | 0.00 | 11.13 | 53.87 | 0.25 | 0.22 | 0.00 | 0.11 | 33.75 | 99.54 |
| | | S.D. | 0.63 | 0.00 | 0.83 | 1.30 | 0.05 | 0.02 | 0.01 | 0.02 | 0.26 | 0.44 |
| | | MAX | 3.88 | 0.01 | 13.72 | 56.06 | 0.31 | 0.26 | 0.03 | 0.15 | 34.24 | 100.74 |
| 5.1 | 0111007 | MINI | 0.06 | 0.00 | 9.10 | 47.96 | 0.12 | 0.17 | 0.00 | 0.06 | 33.06 | 98.20 |
| Dachang | 8111907 | AV. (75) | 0.29 | 0.00 | 11.02 | 52.49 | 0.56 | 0.40 | 0.09 | 0.03 | 33.61 | 98.49 |
| | | S.D. | 0.85 | 0.01 | 1.03 | 1.55 | 0.26 | 0.05 | 0.27 | 0.02 | 0.23 | 1.07 |
| | | MAX | 6.70 | 0.04 | 12.17 | 55.93 | 1.04 | 0.50 | 1.61 | 0.06 | 34.14 | 100.52 |
| | | IVIIINI | 0.00 | 0.00 | 6.20 | 46.72 | 0.09 | 0.30 | 0.00 | 0.00 | 33.05 | 95.26 |

LOD = limit of detection. Value indicating 0.00 = not detected. The number in parenthesis is the number of analyses.

standard deviation (1σ) for minor and trace elements in sphalerite from each of the selected deposits (299 spot analyses in total), as well as in Pb–Sb-bearing minerals from the Huari Huari deposit. Various trends in specific elements and elemental correlations for the deposits are identified, which will be summarized by elements and specific deposits. Figs. 9 and 10; Supplementary Figs. 1 and 2) illustrate relationships between chemical variation and representative analyzed spots of sphalerites and Pb–Sb-bearing minerals, in addition to time-resolved fsLA-ICPMS profiles for the minerals from the selected deposits.

In all datasets, average values for Fe concentrations in sphalerite from each deposit display a narrow variation within a standard deviation. Commonly, black sphalerite indicates higher Fe content than the translucent type. Variation in Fe content inversely correlates with Zn in all samples, attributed to a counterbalance of both elements (e.g., Seifert and Sandmann, 2006). In all deposits, the average Fe concentrations are discriminated into two main clusters composing high and low concentrations. The Toyoha, Akenobe and Potosi deposits display average Fe concentration of <3 wt.% lower than the others. In particular, sphalerites in these three deposits have higher Cd contents, with higher Zn, whereas a correlation between the two elements is regularly negative in the sphalerites from the other deposits (Fig. 8a).

All of the sphalerites contain several thousands of μ g/g Cd. Cadmium contents are also constant: standard deviations are low relative to average values in each deposit, attaining a maximum value in the Bolivar deposit. Furthermore, sphalerites from the Chinese deposits show constant and homogeneous Cd content. Interestingly, cadmium seems to decrease with increasing Fe in Toyoha and Potosi sphalerites, whereas the other sphalerites show either positive or no distinct correlations between the two elements (Fig. 8b).



Fig. 4. Series of images consisting of backscattered image (BI), qualitative microprobe images of In L α (In), Cu K α (Cu) and Sn L α (Sn) for the same area of Potosi samples (98110508B; left column, 98110509; middle column), and Huari Huari sample (HUC; right column). 98110508B: Backscattered image (a1) of assemblage of high- and low-temperature minerals, occurring together with cassiterite (Cas), sphalerite (Sph) and Ag-bearing minerals such as polybasite (Poly) in Potosi deposit. White dots indicate points for quantitative analysis in Table 5. 98110509: Backscattered image (c1) of massive black ore composed of oscillatory-zoned sphalerite from Potosi deposit. White dots indicate points for quantitative analysis in Table 5. HUC: Backscattered image (c1) of massive black sphalerite from Huari Huari deposit. Detail qualitative microprobe images highlighted by white open square are described in Fig. 5. White dots indicate points for quantitative analysis in Table 5. The colored scale bar at the bottom showing relative concentration ranging high (red) to low (blue). Scale bars = 0.1 mm for 98110508B and 98110509, 2 mm for HUC.

Copper signals in individual fsLA-ICPMS spectra are smooth and steady in the majority for the samples (Fig. 9; Supplementary Fig. 1). Copper signals for sphalerites from the Chinese deposits, however, become relatively irregular, probably affected by the presence of sub-micron-sized inclusions within sphalerite (Fig. 10). Average Cu concentrations are detected up to several thousands of µg/g in almost all sphalerites, except for those from the Akenobe and Porco deposits. Standard deviations are typically similar to the average values, indicating a wide variation of Cu in each deposit. In the samples with considerable amounts of In, Cu content positively correlates with Sn (Fig. 9; Supplementary Fig. 1), with the exception of Sn-depleted sphalerite from the Akenobe and Dulong deposits. The highest average Cu concentration is noted in sphalerite with the highest Sn concentration from the Potosi deposit.

Manganese concentrations are generally low (tens or hundreds of $\mu g/g$) in most samples. In contrast, sphalerites from the two Chinese

deposits display a pronounced enrichment in Mn, and have constant average concentrations of Mn of about 2000 μ g/g, with characteristically small standard deviations. This feature may possibly be attributable to the fact that both deposits occur within carbonate-rich strata such as calcareous sedimentary rocks or metamorphic rocks intercalated with marble (Table 2).

Sphalerites from the Toyoha deposit exhibit a wide variation in Ga, showing high standard deviations relative to average values. Average concentration of Ga for almost all sphalerites indicate several hundreds of μ g/g, except for sphalerites from the Akenobe and Dulong deposits which are lower than the minimum analytical detection limit. The behavior of Ga contents for all dataset is similar to that of Ag content.

Sphalerites from the Toyoha and Potosi deposits demonstrate significant Ag enrichment. Similarly to Ga, the higher standard deviations relative to average values imply that Ag is not normally present

Table 5

EPMA analyses of sphalerites and Zn-In minerals from the Potosi and Huari Huari deposits.

| Sample | | 98110508B | | | | 98110509 | | | HUC | | | | | | | | | | |
|------------|---------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Mineral | LOD | Sph | Zn–In | Zn–In | Sph | Sph | Sph | Sph | Sph | Zn–In | Zn–In |
| Point | | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | H1 | H2 | H3 | H4 | H5 | H6 | H7 | H8 | H9 | H10 |
| wt.% | | | | | | | | | | | | | | | | | | | |
| Cu | 0.01 | 2.71 | 3.17 | 0.54 | 0.73 | 2.88 | 1.48 | 0.66 | 0.05 | 8.81 | 10.08 | 10.26 | 0.61 | 5.04 | 1.29 | 0.19 | 3.60 | 9.99 | 10.49 |
| Ag | 0.01 | 0.13 | 0.03 | 0.00 | 0.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.95 | 0.97 | 0.78 | 0.00 | 0.15 | 0.00 | 0.00 | 0.06 | 0.97 | 0.84 |
| Fe | 0.01 | 3.66 | 3.45 | 3.34 | 4.02 | 4.43 | 4.13 | 3.90 | 1.32 | 12.79 | 12.77 | 12.83 | 8.72 | 10.76 | 10.77 | 10.42 | 9.37 | 12.65 | 12.91 |
| Zn | 0.01 | <mark>55.51</mark> | <mark>55.45</mark> | <mark>62.21</mark> | <mark>59.94</mark> | <mark>55.40</mark> | <mark>57.98</mark> | <mark>59.81</mark> | <mark>62.79</mark> | <mark>30.62</mark> | <mark>27.69</mark> | <mark>27.29</mark> | <mark>56.32</mark> | <mark>45.63</mark> | 53.06 | <mark>55.93</mark> | <mark>51.21</mark> | <mark>27.87</mark> | <mark>26.80</mark> |
| Mn | 0.01 | 0.00 | 0.00 | 0.01 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 |
| Cd | 0.01 | 0.13 | 0.15 | 0.12 | 0.04 | 0.17 | 0.17 | 0.19 | 0.46 | 0.24 | 0.22 | 0.20 | 0.31 | 0.34 | 0.33 | 0.49 | 0.35 | 0.17 | 0.00 |
| In | 0.01 | 4.46 | 5.21 | 0.69 | 0.98 | 0.09 | 0.05 | 0.22 | 0.00 | 15.86 | 18.09 | 18.12 | 0.81 | 2.18 | 1.30 | 0.18 | 1.07 | 18.12 | 18.22 |
| Sn | 0.01 | 0.38 | 0.00 | 0.00 | 0.16 | 2.62 | 1.46 | 0.46 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 3.41 | 0.38 | 0.00 | 2.73 | 0.00 | 0.00 |
| S | 0.01 | <mark>33.10</mark> | <mark>32.95</mark> | <mark>33.57</mark> | <mark>33.37</mark> | <mark>32.89</mark> | <mark>33.08</mark> | <mark>32.97</mark> | <mark>32.86</mark> | <mark>31.50</mark> | <mark>31.16</mark> | <mark>31.17</mark> | <mark>33.86</mark> | <mark>33.03</mark> | <mark>33.41</mark> | <mark>33.90</mark> | <mark>33.32</mark> | <mark>31.31</mark> | <mark>31.07</mark> |
| Total | | 100.08 | 100.41 | 100.48 | 99.38 | 98.49 | 98.35 | 98.21 | 97.54 | 100.78 | 100.99 | 100.66 | 100.63 | 100.54 | 100.55 | 101.14 | 101.71 | 101.08 | 100.33 |
| Atomic p | roporti | on (Σ=8 | <mark>;)</mark> | | | | | | | | | | | | | | | | |
| Cu | | 0.16 | 0.20 | 0.04 | 0.04 | 0.20 | 0.08 | 0.04 | 0.00 | 0.58 | 0.66 | 0.66 | 0.04 | 0.32 | 0.08 | 0.00 | 0.24 | 0.66 | 0.66 |
| Ag | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.05 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.04 |
| Fe | | 0.28 | 0.24 | 0.23 | 0.27 | 0.31 | 0.31 | 0.27 | 0.08 | 0.95 | 0.95 | 0.95 | 0.62 | 0.75 | 0.74 | 0.70 | 0.67 | 0.91 | 0.95 |
| Zn | | 3.35 | 3.32 | 3.67 | 3.57 | 3.36 | 3.49 | 3.60 | 3.83 | 1.89 | 1.73 | 1.69 | 3.30 | 2.72 | 3.13 | 3.27 | 3.01 | 1.73 | 1.69 |
| Mn | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cd | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Subtotal | | 3.79 | 3.76 | 3.94 | 3.88 | 3.87 | 3.88 | 3.91 | 3.91 | 3.47 | 3.39 | 3.35 | 3.96 | 3.79 | 3.95 | 3.97 | 3.92 | 3.34 | 3.34 |
| In | | 0.16 | 0.20 | 0.04 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.58 | 0.66 | 0.66 | 0.04 | 0.08 | 0.04 | 0.00 | 0.04 | 0.66 | 0.66 |
| Sn | | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 |
| Subtotal | | 0.16 | 0.20 | 0.04 | 0.04 | 0.08 | 0.04 | 0.00 | 0.00 | 0.58 | 0.66 | 0.66 | 0.04 | 0.20 | 0.04 | 0.00 | 0.12 | 0.66 | 0.66 |
| 5 Total | | 4.06 | 4.03 | 4.02 | 4.07 | 4.06 | 4.07 | 4.07 | 4.10 | 3.98 | 3.96 | 4.00 | 4.03 | 4.02 | 4.02 | 4.04 | 3.99 | 3.99 | 3.99 |
| TOLAI | | 8.01 | 7.99 | 8.00 | 7.99 | ð.01 | 7.99 | 7.98 | ð.0 I | 8.03 | ð.01 | ð.0 I | 8.03 | 8.01 | ð.01 | ð.01 | 8.03 | 7.99 | 7.99 |

LOD = limit of detection. Value indicating 0.00 = not detected. Analyzed points are indicated in Figs. 3 and 4.

in solid solution, but may additionally correspond to sub-micronscale inclusions of Ag-bearing minerals or Pb–Sb-sulfides, even though a smooth and stable signal of Ag is noted for the fsLA-ICPMS profiles for the sample of the Potosi deposit (Fig. 9) and other deposits (Supplementary Fig. 1), suggesting that some Ag may be lattice-bound. In contrast, sphalerites from the Akenobe and Dulong deposits are poor in Ag. Notably, sphalerites from the Akenobe and Dulong deposits are almost totally depleted in Ag, Sn and Ga.

Anomalous Pb and Sb contents in sphalerites in the Toyoha and Potosi deposits have no correlations with Cu–In–Sn, suggesting the presence of sub-micron scale of Pb–Sb-bearing sulfide inclusions as the same manner considered for Ag.

Table 6

| Representative chemical comp | position of pyrargyrite and | l miargyrite in Potosi a | and miargyrite and jamesonite | e in Huari Huari deposits. |
|------------------------------|-----------------------------|--------------------------|-------------------------------|----------------------------|
|------------------------------|-----------------------------|--------------------------|-------------------------------|----------------------------|

| Mineral | | Pyrargyrite | | Miargyrite | | | Jamesonite | | | |
|---------|------|-------------|-------------------------|-------------|-----------------------|-------------|------------|--------------|--------------------------|--|
| Deposit | | Potosi | | Potosi | | Huari Huari | | Huari Huari | | |
| Sample | | 98110507 | | 98110508B | | HUC | | HUC | | |
| Point | LOD | 3 | 10 | 1 | 3 | 8 | 14 | 15 | 17 | |
| wt.% | | | | | | | | | | |
| Cu | 0.01 | 0.18 | 0.11 | 0.01 | 0.08 | 0.04 | 0.02 | 0.01 | 0.00 | |
| Ag | 0.01 | 60.01 | 60.12 | 36.21 | 36.50 | 36.34 | 36.32 | 0.04 | 0.03 | |
| Fe | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.06 | 2.73 | 2.66 | |
| Zn | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.44 | 0.01 | 0.03 | |
| Mn | 0.01 | 0.01 | 0.00 | 0.02 | 0.00 | 0.02 | 0.03 | 0.01 | 0.00 | |
| Cd | 0.01 | 0.24 | 0.23 | 0.18 | 0.18 | 0.17 | 0.14 | 0.04 | 0.05 | |
| Sb | 0.01 | 22.50 | 22.25 | 41.52 | 41.31 | 42.25 | 41.65 | 36.00 | 35.66 | |
| As | 0.01 | 0.05 | 0.05 | 0.18 | 0.09 | 0.13 | 0.13 | 0.00 | 0.00 | |
| Bi | 0.02 | 0.00 | 0.00 | 0.72 | 0.52 | 0.00 | 0.00 | 0.00 | 0.00 | |
| Pb | 0.01 | 0.06 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 39.88 | 40.30 | |
| S | 0.01 | 17.78 | 17.79 | 21.91 | 22.14 | 21.88 | 22.06 | 22.20 | 21.78 | |
| Total | | 100.85 | 100.57 | 100.76 | 100.83 | 100.88 | 100.86 | 100.92 | 100.51 | |
| | | Atomic prop | ortion ($\Sigma = 7$) | Atomic prop | ortion $(\Sigma = 4)$ | | | Atomic propo | ortion ($\Sigma = 25$) | |
| Cu | | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| Ag | | 3.00 | 3.00 | 0.99 | 0.99 | 0.98 | 0.98 | 0.02 | 0.02 | |
| Fe | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.98 | 0.98 | |
| Zn | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | |
| Mn | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| Cd | | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | |
| Sb | | 1.00 | 0.98 | 1.00 | 0.99 | 1.01 | 0.99 | 5.98 | 6.04 | |
| As | | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | |
| Bi | | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | |
| Pb | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.90 | 4.02 | |
| S | | 2.99 | 2.99 | 2.00 | 2.01 | 1.99 | 2.00 | 14.00 | 14.03 | |

LOD = limit of detection. Value indicating 0.00 = not detected (lower than LOD).



Fig. 5. Qualitative microprobe images of ln Lα, Cu Kα, Sn Lα and Ag Lα for the highlighted area in Fig. 4c1. White dots indicate points for quantitative analysis in Table 5. The colored scale bar showing relative concentration ranging high (red) to low (blue). Scale bars = 50 µm.

Even though we have avoided the most In-rich zones in sphalerites when conducting the analysis, In concentrations show a wide variation ranging from several $\mu g/g$ up to thousands $\mu g/g$. Among the data obtained, In enrichment of sphalerite is more obvious in the Huari Huari, Potosi and Bolivar deposits than in the others, being in a good agreement with the high 1000In/Zn values of the ore from these



Fig. 6. Ternary plot of Cu + Ag, Fe + Zn(+ Mn + Cd), and In + Sn of In-rich sphalerites from Potosi and Huari Huari deposits. Left diagram is enlarged the area which is highlighted in right diagram. Dotted lines indicate tie-lines for the series of solid solutions of sphalerite (Sp) – stannite (St) and sphalerite (Sp) – roquesite (Rq).



Fig. 7. Homogeneous compositional images revealed by Zn K α and In L α for translucent brownish to reddish sphalerites (open nicol = ON) from Dulong and Dachang deposits, China. The colored scale bar at the bottom shows relative concentration ranging high (red) to low (blue). Series images from upper to bottom are corresponding to the same areas in sphalerites from Dulong and Dachang deposits, respectively. Scale bars = 0.2 mm.

deposits (Fig. 8c; Table 7). In terms of the range of In concentration, sphalerite from the Akenobe, Dulong and Dachang deposits is distinguished by a narrow variation. In contrast, the In content of sphalerite from the other deposits demonstrates a wide variation and correlates with both Zn and Fe (Fig. 8c, d). In general, the highest In content was obtained from black opaque sphalerite in the oscillatory-zoned sphalerite, which is also enriched in Cu and, to some extent, in Sn (Fig. 4). The lowest concentrations were observed in the translucent sphalerite.

Normally, Cu, In, Sn and Ag concentrations have a higher standard deviation than the average values for each deposit, except for the Akenobe and Dulong deposits which are depleted in Sn, Ag and Ga. In the Sn-poor deposits, analyzed sphalerites exhibit an atomic proportion of Cu to In almost 1:1, as shown in fine-grained black sphalerite in the Potosi deposit.

For the Bolivian tin polymetallic deposits, oscillatory-zoned sphalerite has a large chemical variation, which coincides with its transparency. Black sphalerite zones generally indicate higher Sn and Cu, which are occasionally accompanied with an increase in In and Ag (Fig. 9; Supplementary Fig. 1). In the Potosi sphalerite, indium concentration has an average value of 430 μ g/g and a maximum of 5290 μ g/g. The high-In parts coincide with black sphalerite, which tend to be located at the boundaries between translucent and oscillatoryIn contrast to the above, sphalerites of the Dulong and Dachang deposits (China) have no distinct optical zoning. Indium concentrations are homogeneous, with averages of $1380 \pm 460 \ \mu g/g (1\sigma)$ and $1020 \pm 240 \ \mu g/g (1\sigma)$, respectively. For each analyzed points in sphalerite from the Dachang deposit, the In content is more constant relative to a greater variation in the Sn and Cu contents, where opaque dusty parts are enriched in abundant blebs of chalcopyrite (Fig. 10).

In the Potosi and Huari Huari deposit, high-In sphalerite is generally associated with Ag–Sb- and Pb–Sb-bearing minerals. Among these, we found that jamesonite is remarkably enriched in In, with concentrations ranging from several hundreds to more than 1000 µg/g. Copper, Sn and Ag are also included as minor impurities in jamesonite. Silver-bearing minerals show no anomalous concentration of In, but Au was detected in miargyrite from the Huari Huari deposit (Supplementary Fig. 2; Table 8). Miargyrite from the Potosi deposit is also characterized by elevated concentrations of Bi and Pb.

5. Discussion

5.1. Relationship between In content and occurrence of sphalerite

In spite of our random analysis which sought to avoid extremely high-In sphalerite, 1000In/Zn values of sphalerite are in good agreement with those of the ore grade for each of the selected deposits (Table 7). Especially in the case of the Huari Huari and Bolivar deposits, it is noted that the higher 1000In/Zn ratios in ore harmonize with higher In contents in sphalerite. Furthermore, translucent reddish sphalerite from the Dulong and Dachang deposits is characterized by higher average In concentrations, supporting their moderate 1000In/Zn values in ore. It is thus proven that sphalerite is the principal mineral to account for a broad range of In concentration in ores from the different tin-polymetallic deposits (c.f., Schwarz-Schampera and Herzig, 2002). When comparing the 1000In/Zn ratio between sphalerite and ore grade for each deposit, the deposits dominated by oscillatory-zoned sphalerite are generally lower than the 1:1 line, whereas for deposits composed of homogeneous sphalerite plot around the 1:1 line (Fig. 11). The former case is consistent with the presence of extremely high-In sphalerite which compensates for the difference in 1000In/Zn ratio from that of ore grade (Figs. 4 and 5).

On the basis of microscopic observation, the abundance of In is considerably different between the two sphalerite types; high-In black, opaque, sphalerite and low-In translucent sphalerite in the oscillatoryzoned sphalerite (Figs. 4 and 9; Supplementary Fig. 1), with the exceptions of sphalerite from Dulong and Dachang (Fig. 10). The high-In black sphalerites are generally enriched in Cu and Sn, and occasionally also in Ag (Fig. 9; Supplementary Fig. 1). It is well accepted that the opacity of sphalerite generally depends on the Fe content. Accordingly, enrichment of Cu, Sn, In and Ag in sphalerite is closely related to the presence of black opaque sphalerite, manifesting a positive correlations between the presence of those trace elements with Fe (e.g., Fig. 8d).

5.2. Element substitutions in sphalerite

Based on the analysis via fsLA-ICPMS, representative relations between Cu, Sn, Ag, Ga and In are illustrated in Fig. 12. Comparison of sphalerite trace element concentrations reveals distinct positive and negative correlations for various elements. The observed elemental relations for sphalerite from major tin-polymetallic deposits here are basically in good agreement with previously published data (Cook et al., 2009; Ye et al., 2011).

Table 7

Average concentrations of minor and trace elements in sphalerites from the selected deposits by fsLA-ICPMS analysis.

| | | PD B1 | i |
|---|------------|---------|--------|
| Ore Sphalerite % % µg/g µg/g µg/g µg/g µg/g µg/g µg/g | µg/g | µg/g µg | g/g |
| LOD 0.01 0.01 7 4 2 3 7 1 4 | 4 | 2 1 | |
| Toyoha | | | |
| TYHZn (23) 2.1 0.4 A.V. 63.7 1.7 1940 109 137 406 2670 263 1260 S.D. 1.5 0.8 2680 104 368 1010 1890 507 1410 | 86 80 | 168 n. | d d |
| Ashio (Kajika) | 00 | 155 11. | u |
| ASK3 (32) 1.5 0.7 A.V. 53.6 7.7 3160 54 126 26 4030 356 2150 | n.d | n.d n.e | d |
| S.D. 0.9 0.5 5600 23 71 42 640 603 4530 | n.d | n.d n.o | d |
| AK2307 (26) 0.5 0.3 A.V. 66.4 0.2 432 19 n.d 14 3710 219 n.d | n.d | 8 n. | d |
| S.D. 0.3 0.0 254 6 n.d 11 180 36 n.d | n.d | 9 n. | d |
| Potosi 98110509 (46) 1.4 0.7 A.V 60.4 1.5 9850 17 85 223 1500 430 6780 | 553 | 367 n. | d |
| S.D. 2.3 0.6 5730 10 72 200 900 853 4090 | 484 | 496 n. | .d |
| Huari Huari | | | |
| HUC (60) 11 6.1 A.V. 56.1 5.6 3100 101 116 125 2840 3450 699 SD 2.2 1.3 2560 106 87 129 550 2910 1160 | 22 68 | 9 n.0 | d d |
| Bolivar | 00 | 15 11, | u |
| B1905 (31) 7.4 4.0 A.V. 57.8 4.2 2450 78 249 156 6660 2290 671 | 88 | 13 n. | d |
| S.D. 1.6 0.8 1320 54 111 186 260 1220 487 Porco | 154 | 7 n. | d |
| 98110401 (15) 0.3 0.0 A.V. 55.1 5.2 755 375 35 36 1680 20 618 | n.d | n.d n.e | d |
| S.D. 3.1 1.9 939 226 17 57 460 30 881 | n.d | n.d n.e | d |
| Dulong 112242 (34) 2.2 2.6 A.V. 53.9 6.0 3810 1760 n.d. 14 2000 1380 11 | n d | 7 2 | 0 |
| S.D. 1.3 0.2 4060 280 n.d 9 120 460 0 | n.d | 5 2 | 0 |
| Dachang | | | |
| 8111907 (32) 3.3 1.9 A.V. 53.4 5.7 5250 2260 32 54 4100 1020 3640 S.D. 1.2 0.5 5630 650 15 67 190 240 4810 | n.d n.d | n.d n.d | d d |

LOD = limit of detection. ^a = Zn was measured by EPMA. n. d = not detected (lower than limit of detection).

The measured values more than thousand µg/g are rounded to three significant digits. Values in parentheses are numbers of analyses.

Iron content in sphalerite correlates inversely with Zn across the full dataset, depending on the trade-off between both elements (e.g., Seifert and Sandmann, 2006). In terms of Fe concentration, our dataset can be divided into high- and low-Fe sphalerite by a threshold concentration of around 3 wt.%. The low-Fe sphalerites derive from the Akenobe, Toyoha and Potosi deposits, while the high Fe ones from the other deposits. However, for the Akenobe, Dulong and Dachang deposits, Zn, Fe, Cd and In contents in sphalerite appears to be constant, with only limited variation of these elements (Fig. 8). Sphalerite from the Akenobe and Dulong deposits is characterized by a relative depletion in Ga, Sn and Ag. In addition, for sphalerite from the Akenobe and Dulong deposits, variations of trace

elements such as Cu and Sn are independent of the In content (Figs. 10 and 12). Accordingly, the sphalerites from the three deposits are excluded from the following discussion unless noted otherwise.

The low-Fe sphalerites from the Toyoha and Potosi deposits indicate a wide range of Cd concentration (Fig. 8a, b). For the Potosi deposit, the low-Fe sphalerite population can be separated into high-Cd and low-Cd by a threshold value of 2000 μ g/g; high-Cd sphalerite is depleted in Fe, while the low-Cd variety is Fe-enriched (Fig. 8b). This supports that the Cd content of black sphalerite is lower than that of translucent sphalerite in the Potosi deposit (Table 4). Hence, Cd as well as the Fe content of the low-Fe sphalerite from the Toyoha deposit are lower than the reported

Table 8

| Deposit | Sample | | Ag ^a | Sb | Fe | Cu | Mn | Ga | As | Zn | Cd | In | Sn | Pb ^a | Bi | Au |
|--------------------------|---------------|------|-----------------|--------|------|--------|------|------|------|------|------|------|--------|-----------------|------|------|
| | | | % | % | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g |
| | | LOD | 0.01 | 0.0004 | 160 | 7 | 4 | 2 | 27 | 32 | 7 | 1 | 4 | 2 | 1 | 1 |
| Miargyrite Potosi | | | | | | | | | | | | | | | | |
| | 98110508B (8) | A.V. | 35.7 | 38.2 | 242 | 460 | n.d | n.d | 265 | 105 | 36 | 4 | 20 | 749 | 6530 | - |
| | | S.D. | 0.6 | 1.2 | 70 | 454 | n.d | n.d | 217 | 234 | 14 | 6 | 13 | 388 | 8840 | - |
| Huari Huari | | | | | | | | | | | | | | | | |
| | HUC (9) | A.V. | 36.1 | 42.5 | n.d | 95 | 414 | n.d | - | 33 | 38 | n.d | 11 | 457 | 25 | 38 |
| | | S.D. | 0.3 | 1.4 | n.d | 15 | 58 | n.d | - | 58 | 21 | n.d | 10 | 217 | 45 | 5 |
| Pyrargyrite Potosi | | | | | | | | | | | | | | | | |
| | 98110507 (10) | A.V. | 59.0 | 22.0 | n.d | 722 | n.d | n.d | - | n.d | n.d | n.d | 5 | 25 | n.d | n.d |
| | | S.D. | 0.6 | 0.7 | n.d | 68 | n.d | n.d | - | n.d | n.d | n.d | 4 | 22 | n.d | n.d |
| Jamsonite Huari Huari | | | | | | | | | | | | | | | | |
| | HUC (9) | A.V. | 0.5 | 34.9 | n.d | 24,300 | 186 | n.d | - | 1050 | 79 | 624 | 10,600 | 398,000 | 61 | n.d |
| | | S.D. | 0.8 | 1.6 | n.d | 1200 | 323 | n.d | - | 2730 | 30 | 300 | 5500 | 19,600 | 27 | n.d |

LOD = limit of detection. n.d = not detected (lower than LOD). - = not analyzed.

Values in parentheses are numbers of analyses.

The measured values more than thousand $\mu g/g$ are rounded to three significant digits.

^a = Ag determined via EPMA analysis for miargyrite and pyrargyrite, Pb for jamesonite (LOD = 0.01 wt.%).



Fig. 8. Comparisons of Zn-Cd, Fe-Cd, Zn-In and Fe-In by fsLA-ICPMS analysis for sphalerite from the selected deposits.

value for sample In-1 reported by Cook et al. (2009), but are at a similar order of magnitude with respect to trace elements such as In. In this context, it seems that enrichment in In, Cu, Sn and Ag is not related to a variation in Cd content, but rather to a decrease in Zn and increase in Fe for

the low-Fe sphalerite from the Toyoha and Potosi deposits. This is consistent with a negative correlation between In and Zn (Fig. 8c), and implies an influence from both the coupled substitution $(Zn^{2+}) \leftrightarrow (Fe^{2+})$, as well as complex relationships between In, Cu, Sn and Ag and Zn.



Fig. 9. Individual analysis points with representative fsLA-ICPMS spectra for Zn, Cu, Sn, In and Ag in sphalerite from Potosi deposit (the same area in Fig. 2a). Colored circles in the photograph indicate concentration range of indium at each point. Note black zones in oscillatory-zoned sphalerite are enriched in Sn and Cu, partly In and Ag, while translucent zones are poor in those trace elements. Scale bar = 0.5 mm.



Fig. 10. Individual analysis points with representative fsLA-ICPMS spectra for Zn, Cu, Sn, In and Ag in sphalerite from Dachang (upper image) and Dulong (bottom image) deposit (the same area in Fig. 2h and g, respectively). Upper graph shows fsLA-ICPMS trace element concentration profile of sphalerite from Dachang deposit. The black opaque parts of sphalerite correlate with an increase of trace elements such as Cu and Ag, while uniform concentration is found for In. Scale bar = 0.2 mm.



Fig. 11. Comparison of the 1000In/Zn ratio in sphalerite and ore grade for each deposit.

The direct relationship between Cu and In is obvious for the high-Fe sphalerite, especially for analyzed sphalerite from the Huari Huari and Bolivar deposits (Fig. 12a). This represents a ratio of atomic proportion of Cu to In almost 1:1 which is also observed in the high-In fine-grained black sphalerite of the Potosi deposit. This is consistent with substitution of Cu as Cu⁺ in the sphalerite structure (Cook et al., 2012), supporting charge balance when In is incorporated as In³⁺. The high-Fe sphalerites regularly have a negative correlation between Cd and Zn (Fig. 8a), implying that trace elements such as In and Cu also increase with higher Fe and Cd. The positive correlations between Fe and both Cd and In (Fig. 8b, d) corroborate the correlation between Cu and In, suggesting the following coupled substitutions: $(2Zn^{2+}) \leftrightarrow (Fe^{2+}, Cd^{2+})$ and $(2Zn^{2+}) \leftrightarrow (Cu^+, In^{3+})$.

In this study, it is recognized that analyzed sphalerite with elevated Cu and lower In plot beyond the Cu/In line of ~1 (Fig. 12a). This observation was previously reported for the sphalerite from Toyoha as well as some skarn and massive sulfide deposits; this excess Cu was considered to be caused by sub-micron inclusions of chalcopyrite (Cook et al., 2009; Ye et al., 2011). In addition, Ciobanu et al. (2011)



Fig. 12. Relationships between In and Cu (a), In and Sn (b), In and Ag (c), Ag and Sn (d); Cu and Sn (e), Cu and Ag (f), Zn and Cu + Sn (g), Ga and In (h), Ga and Cu (i) in sphalerite derived from all the fsLA-ICPMS analyses.

show evidence for nanoparticles of laforêtite and other phases in the Toyoha sphalerite and stress the significance of lattice-scale twinning and polytypism in ZnS.

Within the elevated Cu samples, the highest Cu, Sn and Ag contents are observed in low-Fe sphalerite from Potosi (Fig. 12a). They all correspond to the low-Cd black sphalerite zone in the oscillatory-zoned sphalerite from the Potosi deposit (Fig. 9). In addition, these samples have a constant atomic proportion of Cu to Sn about 2:1 (Fig. 12e), supporting EPMA analysis for Potosi sphalerite. Furthermore, the samples showing higher Cu and Sn display no systematic correlation with Zn (Fig. 12g). Judging from these observations, the highest Cu, Sn and Ag samples from the Potosi deposit is likely to result principally from sub-micron inclusions of stannite rather than a possible coupled substitution such as $(3Zn^{2+}) \leftrightarrow (2Cu^+, Sn^{4+})$ which would need to operate if Sn is present as Sn⁴⁺ (e.g., Cook et al., 2009).

Except for the Potosi sphalerites, the elevated Cu samples with the highest Ag, Sn and Cu contents have positive correlations between In and both Cu and Sn (Fig. 12a, b). Moreover, not only Potosi sphalerite but also sphalerite from Toyoha, Ashio and Porco, as well as a sub-population from Dachang, plot close to the 1:1 Sn:Cu line on Fig. 12e. The analyzed sphalerite with elevated Cu shows a negative correlation between Cu + Sn and Zn (Fig. 12g). This suggests that they involve not only the substitution $(3Zn^{2+}) \leftrightarrow (2Cu^+, Sn^{4+})$, but also $(2Zn^{2+}) \leftrightarrow (Fe^{2+}, Cd^{2+})$ and $(2Zn^{2+}) \leftrightarrow (Cu^+, In^{3+})$, as observed in high-Fe sphalerites.

In contrast, the Ag content of the sphalerites display a scattered relationship with In (Fig. 12c), especially in the case of those with elevated Cu from Toyoha, Ashio, Potosi and Porco. Although the Cu and Sn contents in sphalerite might be related to the coupled substitution $(3Zn^{2+}) \leftrightarrow (2Cu^+, Sn^{4+})$, the inconsistent correlation between Ag and In is more likely to relate to another coupled substitution. This raises the possibility of supplementary coupled substitutions involving Zn, In, Cu, Ag and also Sn, such as $(2Zn^{2+}) \leftrightarrow (Cu^+, In^{3+})$ and $(3Zn^{2+}) \leftrightarrow (Cu^+, Ag^+, Sn^{4+})$. The latter coupled substitution is consistent with the positive correlation between Ag and both Cu and Sn (Fig. 12d, f), which results in a greater deficiency of In in the relationship between Zn and In for the Toyoha, Ashio, Potosi and Porco sphalerites than the Huari Huari and Bolivar sphalerites (Fig. 8c). Furthermore, sphalerite from the Dachang deposit is likely to show a similar manner of interrelations among those elements. We believe therefore that various combinations of the coupled substitutions $(3Zn^{2+}) \leftrightarrow (2Cu^{+})$ Sn^{4+}), $(2Zn^{2+}) \leftrightarrow (Cu^+, In^{3+})$ and $(3Zn^{2+}) \leftrightarrow (Cu^+, Ag^+, Sn^{4+})$ would account for the Cu, Sn and Ag contents within a wide range of In concentrations in the elevated Cu samples from Toyoha, Ashio, Potosi, Porco and Dachang. On the other hand, sphalerite from the Akenobe and Dulong deposits also shows a positive correlation between Cu and both In and Ag, but does not indicate associations these elements and Sn due to their relative depletion of Sn. It is considered that the composition of sphalerite in these two deposits is essentially governed by the single coupled substitution $(2Zn^{2+}) \leftrightarrow (Cu^+ \text{ or } Ag^+, In^{3+}).$

Sphalerite from Toyoha, Ashio, Potosi and Porco displays a positive correlation between In and Ga (Fig. 12h); the Ga content in sphalerite also tends to correlate with Cu. The wide variation in In of sphalerite also corroborates with Ga content, resulting in the proposed coupled substitution $(2Zn^{2+}) \leftrightarrow (Cu^+, Ga^{3+})$. This may also contribute to the substitution system in the Toyoha, Ashio, Potosi and Porco sphalerites.

5.3. Ag content in sphalerite

The Toyoha and Potosi sphalerites containing the highest concentrations of Cu, Sn and Ag are also markedly enriched in Pb and Sb (Table 7). We interpret that the presence of sub-micron-scale inclusions of Ag- and Pb–Sb-bearing sulfides contribute to the highest Ag content rather than the coupled substitutions discussed above such as $(3Zn^{2+}) \leftrightarrow (Cu^+, Ag^+, Sn^{4+})$. Silver- and Pb–Sb-bearing sulfides are typically widespread in tin-polymetallic deposits. The shallower part of such deposits are commonly enriched in Ag, as observed in the Potosi deposit which had high grade Ag-ores (30–40% Ag) mined out from the shallower oxidized zone (Ishihara et al., 2011b and references therein). Silver-bearing minerals such as galena, pyrargyrite, acanthite and stephanite are concentrated in upper levels of the Porco deposit. In addition to the Bolivian deposits, Toyoha is regarded to have formed in a shallower (volcanic) zone, compared with the (deeper) granitic intrusion-related Chinese deposits (Table 2). Despite a restricted number of data, the average Ag concentrations appear to decrease with formation depth (Fig. 13), with the Ag content in sphalerite lowest for the intrusion-related Dulong deposit. High-Ag sphalerite generally shows oscillatory zoning and occurs in typical vein type deposits such as Toyoha, whereas low-Ag sphalerite in the Chinese deposits occurs in the massive or replacement orebody. Considering all these data, the Ag content of sphalerite from tin polymetallic deposits may serve as a key element to discriminate depth of formation ranging from plutonic to subvolcanic environments. In the Potosi and Huari Huari deposit, jamesonite, associated with Ag- and Pb-Sb bearing minerals, is enriched in In, Cu, Sn and Ag, whereas Ag-bearing minerals show no anomalous In values. Thus, not only sphalerite but also Pb-Sb minerals such as jamesonite may be potential carriers of indium, in the high-Ag, shallow environment of the deposits.

5.4. Magmatic contribution for chalcophile elements

In general, the igneous rocks associated with the Japanese metal deposits are characterized by the following δ^{34} S systematics. Granitoids in the magnetite-series belt usually display positive δ^{34} S values, whereas those in the ilmenite-series belt are normally negative (Ishihara and Sasaki, 2002; Ishihara et al., 2000; Sasaki and Ishihara, 1979). An average δ^{34} S value for sphalerites is + 5.9‰ for Toyoha (Hamada and Imai, 2000). Ohta (1995) interpreted the mineralization of the Toyoha deposit as being derived from magnetite-series magmatic fluids with an additional contribution of reducing agents that originated in basement pelitic rocks. In Ashio, replacement ore including sphalerite and pyrrhotite has an average δ^{34} S value of +2.5% for the Kajika orebody (Ishihara et al., 2006), which is consistent with the recognition that this deposit is affiliated with the Cenozoic magnetite-series belt. The Akenobe deposit, however, shows smaller negative values of δ^{34} S (-1.9‰) than those in the peripheral deposits in the ilmenite-series belt (Ishihara and Sasaki, 2002). An explanation of this anomaly is beyond the scope of present study but we nevertheless speculate that Sn-poor sphalerite in earlystage base metal quartz veins in Akenobe may have formed from a unique ore-forming fluid which originated from a different source to that which contributed to the later stage Sn–W quartz vein (e.g., Ishihara et al., 1981). The Japanese deposits treated here, except for the Akenobe deposit, could have a genetic relation to magnetite-series magmatism.



Fig. 13. Relationships between the Ag content of sphalerite and depth of formation of the selected tin-polymetallic deposits estimated by geological features and the corresponding depth by microthermometry. Depth data from Shimizu and Morishita (2012) for Toyoha, Sillitoe et al. (1975) for Potosi, and Pasava et al. (2003) for Dachang.

On the other hand, sulfides from the Bolivian and Chinese deposits show a wide variety of δ^{34} S values (e.g., Pasava et al., 2003; Sugaki et al., 1990). They normally have positive δ^{34} S values, concordant with a potential magnetite-series affinity. However, for ³⁴S enrichment in the Dachang deposit, both magmatic sulfur and sulfate from the carbonaterich strata are possible sources (Ishihara et al., 2011a). Accordingly, it is difficult to directly apply the δ^{34} S systematics for the Bolivian and Chinese deposits. Based upon ore vein mineral assemblages, the tinpolymetallic ore deposits generally contain pyrrhotite, thus indicating an intermediate character between the magnetite-series and ilmeniteseries, and formation temperatures in the range between 300 °C and 400 °C (Table 2). Furthermore, coupled substitutions involving Cu-In and Cu-Ag-Sn in sphalerite are prominent for the selected deposits. With respect to indium, reconnaissance studies of the Dachang deposit (Ishihara et al., 2009) have not shown anomalous amounts of In in the sedimentary rocks. These data thus imply an oxidized magma, such as that associated with magnetite-series granitoids, is also important for enrichment of In and other elements, because of ability to transport sulfur and chalcophile elements (Fig. 14). We consider that conditions for magma emplacement and associated mineralization for the tinpolymetallic deposits are slightly higher oxygen fugacity than those of tin-mineralization related to granitic magmatism. In the Japanese Island arc, the possible presence of reducing sediments such as those in accretionary terrains, intruded by various deep oxidized magmas, may explain the abundance of sulfur, Sn and chalcophile elements such as Cu and In.

6. Concluding remarks

-5

-10

-15

-20

-25

-30

-35

300

Log fO₂ (atm)

Major and trace elements were measured using EPMA and fsLA-ICPMS on a large sample suite of sphalerites from a number of

Cu + Au deposits

Porphyry



400

Sn deposits

500

Tin polymetallic deposits

600

700 800 900

1100

tin-polymetallic deposits. This dataset helps constrain the traceelement distribution in In-bearing sphalerite and its relationship with the 1000ln/Zn ratio in bulk ore.

As previous studies confirmed, sphalerite is the principal mineral to account for a broad range of In concentration in ores from tin-polymetallic deposits. The 1000In/Zn ratios in sphalerite are in good agreement with those of the ore grade for each of the selected tin polymetallic deposits. In particular, the Akenobe, Dulong and Dachang deposits, which are characterized by sphalerite with a homogeneous In content, have similar 1000In/Zn ratio in sphalerite as deposit ore grade. In such cases, the 1000In/Zn ratio in sphalerite could be an indicator for the overall In grade of the deposit. On the other hand, the deposits dominated by oscillatory-zoned sphalerite generally have lower 1000In/Zn ratio than the ore grade, resulting from the additional presence of extremely In-rich minerals.

Indium-bearing sphalerites show various types of substitutions. The dominant substitution mechanisms are $(2Zn^{2+}) \leftrightarrow (Cu^+, In^{3+})$ and $(3Zn^{2+}) \leftrightarrow (2Cu^+, Sn^{4+})$ in the high-Fe sphalerite. Those two substitutions seem to be end-members in a more complex spectrum of inter-relationships between Cu and In. The former substitution is apparent in the Huari Huari and Bolivar deposits, whereas the latter one is prominent in the Toyoha, Ashio, Potosi, Porco and Dachang deposits. The Akenobe and Dulong sphalerites are dominated by the coupled substitution of $(2Zn^{2+}) \leftrightarrow (Cu^+ \text{ or } Ag^+, In^{3+})$. Silver could preferentially substitute in the Cu site, contributing to the coupled substitutions $(3Zn^{2+}) \leftrightarrow (Cu^+, Ag^+, Sn^{4+})$ and $(2Zn^{2+}) \leftrightarrow (Cu^+ \text{ or }$ Ag⁺, In³⁺). Occasionally, sub-micron inclusions such as stannite and Pb-Sb-bearing sulfides can occur in sphalerites, these will also contribute to the high Cu-Sn- and Ag-contents, respectively. The coupled substitutions containing Cu-In and Cu-Ag-Sn in sphalerite are prominent for the selected deposits. Based on the published sulfur isotope data, the trace elements in sphalerite imply an oxidized magmatic source such as magnetite-series granitoids. This may be of prime importance for enrichment in In and other elements. The In enrichment in the Japanese tin-polymetallic deposits may be linked to the presence of reducing sediments such as accretionary terrains that were intruded by various deep oxidized magmas supplying sulfur and chalcophile elements. In addition, the Ag content of sphalerite may be a possible indicator of formation depth in sub-volcanic to plutonic environments when associated with ilmenite-series (and partly magnetite-series) granitoids.

Sphalerite has historically been the main and only target for In recovery among deposits enriched in Zn (Cook et al., 2011b). At present, there are only few available data regarding trace elements such as In and Au in Pb–Sb-bearing minerals from tin-polymetallic deposits. An enrichment of In in jamesonite, and potentially other sulfosalts, as well as enrichment of Bi and Au in miargyrite, should at least be considered to achieve maximum recovery of these trace elements during processing. Cook et al. (2011c) reported that other minerals, including bornite and chalcocite, can incorporate Bi and Ag. Although more data are required to provide coherent evidence, the constant and homogeneous concentrations of In, Bi and Au in these minerals imply that they are probably in solid solution rather than as nano-scale inclusions.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.oregeorev.2013.01.010.

Acknowledgments

The authors acknowledge financial support via a Research Grant from the Institute for Geo-resources and Environment, AIST. Maria Florencia Marquez-Zvalia and Xiaofeng Li are thanked for guiding our fieldwork and sampling in Bolivia and China, respectively. We are grateful to Yoshiaki Kon for skillful technical assistance with analysis via femtosecond LA-ICPMS. This manuscript was considerably improved by valuable and constructive comments by reviewers Nigel Cook and Shoji Kojima and Ore Geology Reviews Associate Editor Cristiana Ciobanu.

Appendix A. Summary for limit of detection of fsLA-ICPMS and EPMA analyses

| Element | | Mn55 | Fe57 | Cu63 | Zn66 | Ga69 | As75 | Ag107 | Cd111 | In115 | Sn118 | Sb121 | Au197 | Pb208 | Bi209 |
|---------|------|------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g | µg/g |
| LOD | | 4 | 160 | 7 | n.d. | 2 | 27 | 3 | 7 | 1 | 4 | 4 | 1 | 2 | 1 |
| EPMA | | | | | | | | | | | | | | | |
| Element | S | Mn | Fe | Cu | Zn | Ga | As | Ag | Cd | In | Sn | Sb | Au | Pb | Bi |
| | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| LOD | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.02 |

n.d. = not determined.

Appendix B. Analyzed data by fsLA-ICPMS for NIST SRM 610 compared with the representative values

| | | This stu | ıdy | | NIS | ST ¹ | Jochum et al. (2011) ² | | |
|-----------|------|---------------------|------------|------------|--------------|-----------------|-----------------------------------|-------------------------|--|
| Element | | Conc. error (1σ) | | RSD (%) | V. | U. | Overall means | Uncertainty of mg range | |
| Mn55 | µg/g | 436 | ± 17 | 3.9 | 457 | ± 55 | 444 - | ±13 | |
| Fe57 | µg/g | 458 | ± 19 | 4.1 | 458 | | 458 ± 9 | | |
| Cu63 | µg/g | 431 | ± 13 | 2.9 | 444 | ± 4 | 441 - | ±15 | |
| Ga69 | µg/g | 441 | ± 10 | 2.3 | | | 433 - | ±13 | |
| As75 μg/g | | 316 | ± 15 | 4.6 | 340 | ± 20 | 325 ± 18 | | |
| Ag107 | µg/g | 242 | 242 ± 6 | | $268\pm\!29$ | | 251 ± 9 | | |
| Cd111 | µg/g | 261 | ± 8 | 2.9 | 244 | ± 22 | 270 - | ±16 | |
| In115 | µg/g | 445 | ± 11 | 2.5 | | | 434 | ±19 | |
| Sn118 | µg/g | 399 | ± 13 | 3.1 | | | 430 - | 29 | |
| Sb121 | µg/g | 371 ± 12 | | 3.1 | 415 ± 3.7 | | 396 ± 19 | | |
| Pb208 | µg/g | 433 ± 11 | | 2.4 | 426 | | 426 ± 1 | | |
| Bi209 | µg/g | g 360 ± 12 | | | | | $384\!\pm\!26$ | | |

1 = NISTcertified and information values (V.) with uncertainties (U.) are indicated in May et al. (2000).

2=Overall mean with uncertainty is unweighted mean of all results in Jochum et al. (2011).

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