

# Indium, germanium and gallium in volcanic- and sediment-hosted base-metal sulphide deposits



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## 1. Introduction

Indium (In), germanium (Ge), and gallium (Ga) have unique chemical and physical properties. This makes them critical for a wide variety of high technology, pharmaceutical, metallurgical and chemical industries. This extended abstract consists of three parts. The first part covers In, Ge, and Ga in terms of their physical and chemical properties, ore mineralogy and uses. The second part summarizes available information on global reserves and resources and production. The third part introduces major deposit-types from which In, Ge, and Ga are recovered, focusing on volcanic-hosted massive sulphide (VHMS) and sediment-hosted massive sulphide (SHMS) deposits. For the purpose of this paper, SHMS deposits include syngenetic or early diagenetic sedimentary exhalative (SEDEX), Mississippi Valley-type (MVT), and Kipushi-type deposits.

## 2. Physical and chemical properties, mineralogy and uses

### 2.1. Indium

Indium is a silvery white, soft (1.2 on the Mohs scale), malleable, and ductile post-transition metal. It is in period 5, group 13 of the Periodic Table, having an average atomic mass of 114.818. The melting point of In is 156.60°C, and its liquid density is 7.02 g/cm<sup>3</sup> at that temperature (Hammond, 2008). Indium is not oxidized in air at ambient temperatures (Schwarz-Schampera and Herzig, 2002). The addition of In generally increases strength, corrosion resistance, and hardness of metals and metal alloys. Indium has high plastic properties even at freezing temperatures (Hammond, 2008; Mercer, 2105).

Relative to other metallic elements, In is rare. The average continental crust contains about 0.05 ppm In; the average oceanic crust contains about 0.072 ppm In (Rudnick and Gao, 2003; Schwarz-Schampera, 2014). Of the 12 indium-bearing minerals that have been discovered, roquesite (CuInS<sub>2</sub>) is the most important; it represents a trace component in ore-forming minerals (Schwarz-Schampera and Herzig, 2002).

Indium substitutes for elements with similar ionic radii in base-metal sulphides, especially those having tetrahedral coordination. High In concentrations can be detected in zinc and copper sulphides, of which sphalerite is the most important for global In production. Other carriers are chalcopyrite,

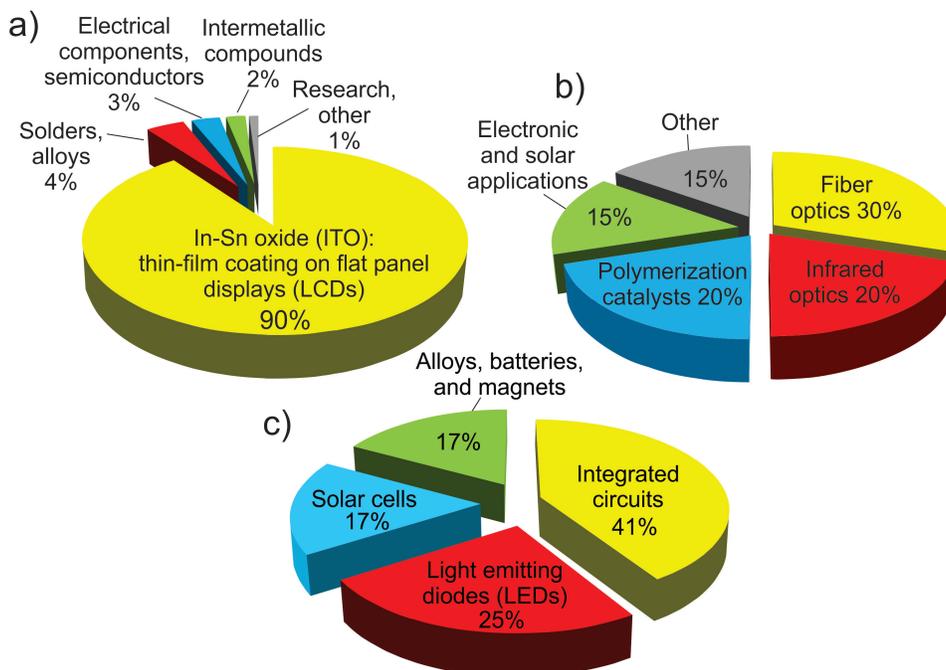
stannite, tin-sulfosalts, tennantite, and cassiterite. Indium is incorporated into these minerals mainly as nano- and micro-scale mineral inclusions (e.g., roquesite inclusions in sphalerite, chalcopyrite, and other sulphides), solid solution through a diadochic replacement of zinc, and in the lattice of tetrahedral-coordinated sulphides. In sphalerite, In is frequently incorporated into the mineral structure via a simple coupled substitution  $2Zn^{2+} \leftrightarrow Cu^{+} + In^{3+}$ .

The principal industrial application of In is in In-Sn oxide (ITO) as a thin-film coating for electronic devices (Fig. 1a). It is also used in alloys and solders, electrical components and semiconductors, and intermetallic compounds (Polinares, 2012).

### 2.2. Germanium

Pure Ge is a hard (7.6 on the Mohs scale), lustrous, greyish white, brittle semi-metal (metalloid). It is an important semiconductor that has many useful applications in high-technology industry (Hammond, 2008; Berger, 2008). Germanium is located in period 4, group 14 of the Periodic Table, and has an average atomic mass of 72.64. The melting point of Ge is 938.25°C, and its liquid density at that temperature is 5.60 g/cm<sup>3</sup> (Hammond, 2008).

Germanium is more common in the Earth's crust than In. It has concentrations of about 2-2.4 ppm in continental crust and 1.5 ppm in oceanic crust (Taylor and McLennan, 1985; Ketrin and Yudovich, 2009). Germanium is present in trace amounts in most rock types because of its siderophile, lithophile, chalcophile, and organophile natures. It does not occur as a native metal in nature. Approximately 30 minerals are known to contain Ge, and many are sulphides. Ge is a substituting element in zinc sulphide structures (e.g., up to 3000 ppm in sphalerite and wurtzite) and copper sulphides (e.g., up to 5000 ppm in enargite, tennantite, bornite, and chalcopyrite) (Höll et al., 2007; Melcher and Buchholz, 2014). Germanium is also present as a substituting element in silicates (e.g., up to 4000 ppm in willemite ZnSiO<sub>4</sub>; up to 700 ppm in topaz), oxides (e.g., up to 7000 ppm in hematite), hydroxides (e.g., up to 5310 ppm in goethite), phosphates, arsenates, vanadates, tungstates, and sulphates (Höll et al., 2007; Melcher and Buchholz, 2014).



**Fig. 1.** **a)** The main end-uses of indium in 2014. Data from Polinares (2012). **b)** The main end-uses of germanium in 2014. Data from Guberman (2015). **c)** The main end-uses of gallium in 2014. Data from European Commission (2015).

Germanium is predominantly used in fiber optics, infrared optics, polymerization catalysts, electronic and solar applications, and other uses such as phosphors, metallurgy and chemotherapy (Fig. 1b; Guberman, 2015).

### 2.3. Gallium

Gallium is a soft, silvery blueish metal, located in period 4, group 13 of the Periodic Table, having an average atomic mass of 69.723 (Hammond, 2008). Solid gallium fractures conchoidally like glass, and exhibits an unusually large liquid range as it has a melting point of 30°C and a boiling point of 2204°C (Butcher and Brown, 2014). This provides the metal with an interesting property, that a solid piece of Ga will liquefy when placed in one's hand (Moskalyk, 2003). The liquid density of Ga at melting point temperature is 6.08 g/cm<sup>3</sup> (Hammond, 2008).

Elemental Ga does not occur in nature, but occurs as Ga(III) compounds that are mostly present in trace amounts in sphalerite and in bauxite (Butcher and Brown, 2014). Its abundance in the Earth's crust is approximately 19 ppm (Butcher and Brown, 2014).

Gallium can combine with a wide variety of elements to produce bromides, chlorides, hydrides, iodides, nitrides, oxides, selenides, sulphides, and tellurides (Handbook of Chemistry and Physics, 2015). Gallium arsenide (GaAs) and gallium nitride (GaN) are valuable compounds presently employed in advanced semiconductors for integrated circuits (ICs), light emitting diodes (LEDs), and solar cells. Other uses are in medical equipment such as alloys, batteries, and magnets (Fig. 1c; European Commission, 2015).

## 3. Resources, reserves and production

### 3.1. Indium

Indium is a by-product of smelting polymetallic base-metal ores, primarily zinc and to a lesser extent, tin and copper. In such ore concentrates, the In content is about 70 to 200 ppm, but may reach values of 800 ppm (Schwarz-Schampera, 2014). About 95% is produced as a by-product from zinc sulphide concentrates with elevated Cu contents at or above 2%. The rest (5%) is extracted from the residues of copper and tin treatment (Schwarz-Schampera, 2014; Werner et al., 2015).

Reliability of global In resource estimates is questionable as details relating to trace metal concentrations in sulphide deposits are not commonly reported by the mining industry. However, it can be estimated from Zn and Cu resources worldwide. By assuming Zn reserves of 250 Mt and 50 grams of In per tonne of Zn, Schwarz-Schampera (2014) projected global resources of 95,000 tonnes and reserves of 12,500 (Table 1). A similar estimate was calculated from global Cu resources.

Large mines with In-bearing ore are in production on all continents with the exception of Antarctica. Globally, zinc concentrates were the principal source of primary In, with world production of primary In estimated at 640 tonnes in 2011 (Tolcin, 2012).

Global In refinery production in 2014 was estimated at 819 tonnes (Fig. 2a; Tolcin, 2015). The largest producers of refined In are China (420 tonnes), South Korea (150 tonnes), Japan (72 tonnes), Canada (65 tonnes), France (48 tonnes), and Belgium (30 tonnes). Some of these countries, such as Belgium, do not have significant In-bearing ore deposits (Schwarz-Schampera, 2014).

**Table 1.** Calculated global resources and reserves of indium in tonnes. From Schwarz-Schampara (2014).

	Resources	Reserves
Zinc ores	95,000	12,500
Copper ores	30,000	6,300
Total	125,000	18,800

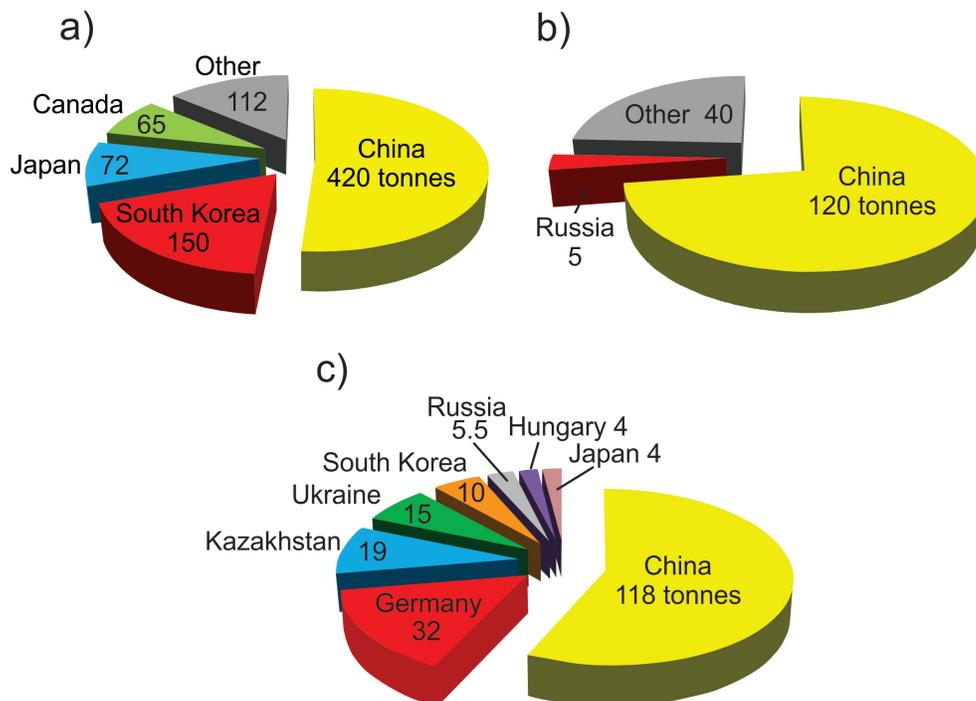
### 3.2. Germanium

Germanium is extracted mainly as a by-product of mining zinc sulphide-rich ores. It comes from sphalerite concentrates containing 50 to 3000 ppm Ge (Sinclair, 2014). Current production mostly comes from SHMS deposits in China (Huize, Jinding and Fankou), the United States (Red Dog SEDEX deposit, Alaska; and MVT deposits of the Elmwood-Gordonsville district, Tennessee) and the Democratic Republic of the Congo (Kipushi deposit). The overall Ge grades in these deposits range from 10 to 300 ppm, for total Ge resources of approximately 5400 tonnes (Bonnet et al., 2014; Melcher and Buchholz, 2014). Germanium is also extracted from coal ash in China, Russia, Ukraine, and possibly Uzbekistan (Melcher and Buchholz, 2014). Germanium content of coal ranges from 30 to 1043 ppm and can be enriched 5- to 10-fold in the ash (Frenzel et al., 2014).

Global Ge resource and reserve data are inconsistent because Ge concentrations in many deposits are not properly reported.

Frenzel et al. (2014) estimated that the minimum amounts of recoverable Ge contained in proven reserves of zinc sulphide ores (at grades in excess of 100 ppm in sphalerite) and coals (in excess of 200 ppm), given current processing technologies, is at least 122,000 tonnes (~10,000 tonnes in zinc ores and ~112,000 tonnes in coal). Melcher and Buchholz (2014) published a compilation of combined reserves and resources for producing mines and exploration base-metal, lignite and coal projects around the world. The total combined reserves and resources are estimated at around 35,903 tonnes of Ge, with approximately 11,000 tonnes coming from the sulphide deposits and associated slags, and 25,000 tonnes coming from the Ge-rich coal and lignite deposits.

The world refinery production of Ge in 2014 was about 165 tonnes (this doesn't include data from the United States; Guberman, 2015), and most of it comes from China (Fig. 2b). In China, both zinc-smelter residues and coal are used. In Canada, another major supplier, production is from zinc ores only. The rest of the world's refinery production comes from Russia, the United States, Spain, India, Finland, and Australia (Mikolajczak, 2011; Melcher and Buchholz, 2014; Guberman, 2015). In addition to primary Ge production and refining, Ge is also recycled from scrap (infrared optics, fibre optics, electronic and solar electrical products, and polymerization catalysts) in China, Russia, Belgium, the United States, and other countries (Guberman, 2015).



**Fig. 2.** a) Global indium refinery production in 2014 per country (data from Tolcin, 2015). b) Global germanium refinery production in 2014 per country (data from Guberman, 2015). c) Estimated world annual primary gallium production for 2010 per country (data from Roskill Information Services Ltd., 2011).

### 3.3. Gallium

Globally, most primary Ga is recovered as a by-product of bauxite and, locally, of zinc ore processing. Recovery rates are not in the public domain but are considered to be low. Therefore, an estimate of current global Ga reserves and resources comparable to In and Ge is difficult to make (Jaskula, 2015). However, because almost all Ga is extracted as by-product during beneficiation of bauxite, Ga reserves in bauxite deposits are estimated at 1.36 Mt and reported resources are probably in a 2.75 to 3.75 Mt range (Dittrich et al., 2011).

The world primary Ga production in 2014 was estimated at 440 tonnes (Jaskula, 2015; production data per country in 2014 are not available), more than double the figure of about 205 tonnes for 2010 (Fig. 2c; Roskill Information Services Ltd., 2011). China, Germany, Japan, and Ukraine were the leading producers in 2014; countries with lesser output were Hungary, South Korea, and Russia. Kazakhstan, reported as a leading producer in 2012, did not produce any primary Ga in 2013, and it is uncertain if it had production in 2015.

Refined Ga production for 2014 was estimated to be 170 tonnes (Jaskula, 2015). China, Japan, the United Kingdom, the United States, and possibly Slovakia were the principal producers of refined Ga. Gallium was recycled from scrap in Canada, Germany, Japan, the United Kingdom, and the United States.

### 4. Major indium-bearing deposit types with focus on volcanic- and sediment-hosted Zn-Pb deposits

Indium is reported from a variety of deposit types, including VHMS, SHMS, polymetallic epithermal vein-breccia-stockwork, porphyry Cu (+/-Zn-Pb), polymetallic vein (+/-Sn), vein-stockwork Sn-W, and skarn (Fig. 3). It is found primarily in Zn ores with a high Cu content, and in Sn ores. This section focuses on two of the main base-metal deposit types, VHMS and SHMS, that contribute to the bulk of identified In resources.

Examples of In-rich VHMS deposits are those of the Iberian Pyrite Belt in Spain and Portugal (e.g., Neves Corvo), Kidd Creek, Brunswick No.12 and Heath Steele deposits in Canada, and Gaiskoye deposit in Russia (Fig. 3).

In VHMS deposits, recoverable concentrations of In are commonly associated with significant amounts of Ag, Sn, Bi, Co, and Se, which can be important by-products. In many deposits, In exhibits a positive correlation with Zn, and Sn and, locally, with Cu. The presence of Bi, Co and In in a deposit typically indicates elevated formation temperatures. Most of the In is present in the crystal lattice of sphalerite and chalcopyrite, and other sulphides (Cook et al., 2009; 2011). Some of it can also occur as mineral inclusions, such as roquesite, which may be present as a trace component in sphalerite- and chalcopyrite-rich ores.

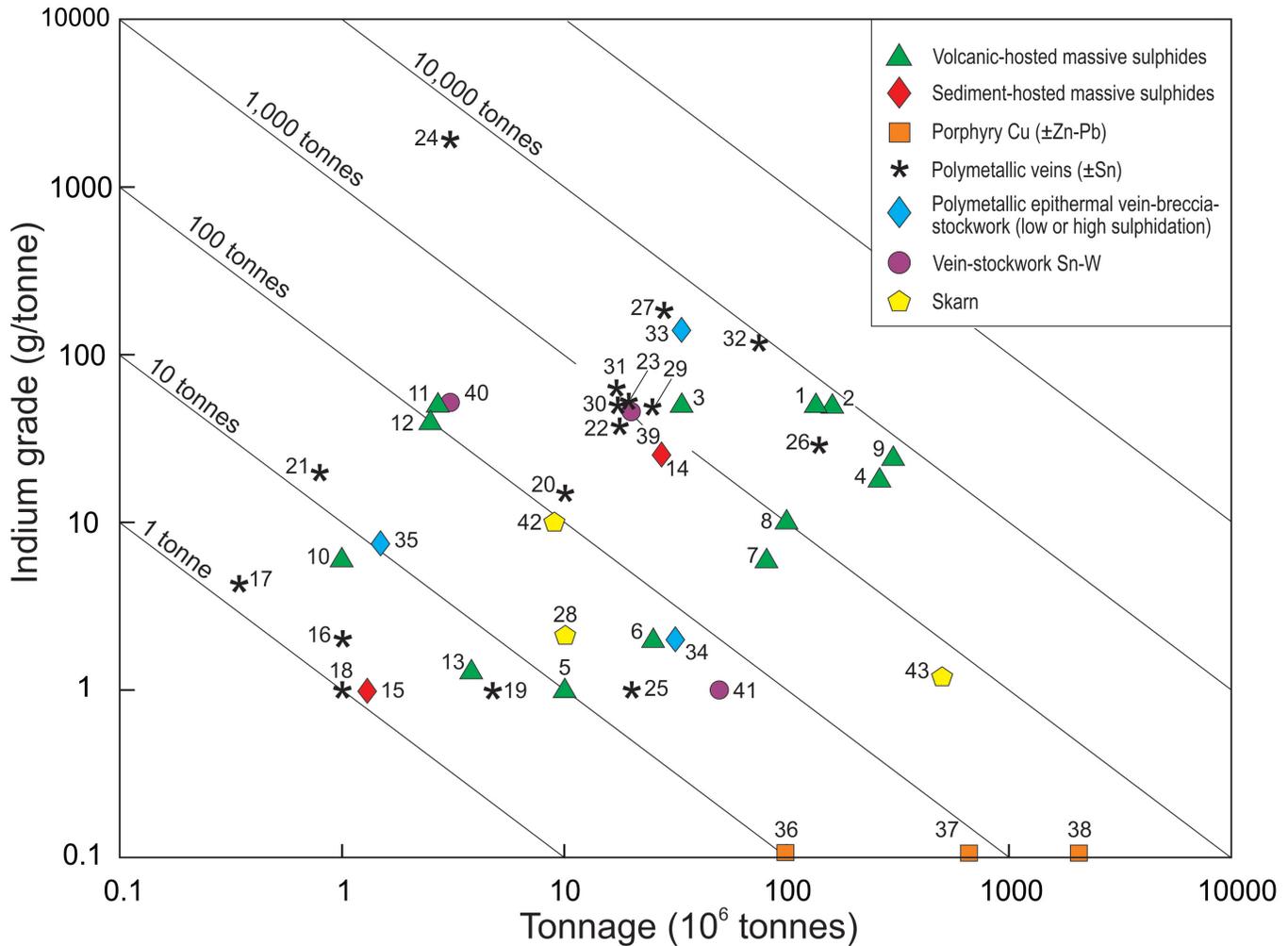
Indium contents in VHMS ores vary from 1 to 320 g/t (Werner et al., 2015), but can be higher in some deposits (e.g., Neves Corvo). At the Kidd Creek deposit, the zinc concentrate had an average of 270 ppm In (Pinto et al., 2014), and annual indium production was 50 tonnes of In metal before the closure

of a smelter in Timmins, Ontario in 2010 (Schwarz-Schampera, 2014). Roquesite in massive chalcopyrite and chalcopyrite stringer ores is estimated to account for about 70% of the bulk In in the deposit; the remainder occurs as solid solution in massive sphalerite (Hannington et al., 1999). At the Brunswick No.12 deposit, In values were associated with sphalerite and chalcopyrite. The zinc concentrate contained concentrations of 400 ppm In and the copper concentrate had 200 ppm In (Werner, et al., 2015). At Neves Corvo, In is present as minor element in the structure of major minerals such as sphalerite, chalcopyrite, stannite group minerals, and tetrahedrite-tennantite group minerals. The highest In grades are observed in the zinc-rich ores at the Graça and Lombador orebodies and in the copper-zinc-rich ores of the Zambujal orebody (Pinto et al., 2013). Overall, in all orebodies of the Neves Corvo deposit, In grades vary between 20 to 1100 ppm and In, Cu, and Sn are positively correlated (Carvalho et al., 2014), especially in the bornite facies of massive cupriferous ores and stringer zones. This contrast with other In-bearing VHMS deposits where In and Zn are positively correlated.

In SHMS deposits of MVT and SEDEX types, In can be an important by-product of Zn-Pb ( $\pm$ Ag)-rich sulphides. However, SHMS deposits typically have lower In concentrations than VHMS deposits. Examples of SHMS deposits with high In content are Red Dog in the United States, Broken Hill and Hyc in Australia, Rammelsberg in Germany, and Polaris in Canada. At the Rammelsberg SEDEX deposit, the highest In values were found in chalcopyrite replacement mineralization of bedded sphalerite ore, which had In values between 180 and 300 ppm (Schwarz-Schampera and Herzig, 2002). At the Polaris MVT deposit, In content was on average 100 ppm in the zinc concentrate (Pinto et al., 2014). Sphalerite from the Pine Point MVT deposit in Canada has variable In content (0 to 890 ppm; avg. 120 ppm), and sphalerite from the Robb Lake deposit in the northern Canadian Cordillera has similar In content of 0 to 750 ppm (avg. 167 ppm) (Paradis, unpublished data). However, sphalerite from other MVT deposits of the southern Canadian Cordillera has much lower In values (0 to 167 ppm; avg. 23.5 ppm). In all the Canadian MVT deposits, no positive correlation was observed between In and Zn, Fe, and Cu; instead, In seems to correlate with Sn, Ag, Ga, Ge, and Cd (Paradis, unpublished data).

### 5. Major germanium-bearing deposit types with focus on sediment-hosted Zn-Pb deposits

Germanium is widely distributed but recovered mainly from SHMS deposits (SEDEX, MVT, and Kipushi-type). The other main source of primary Ge production is the ash produced from lignite deposits. Germanium content of lignite ranges from 30 to >1000 ppm and can be enriched 5- to 10-fold in the ash (Frenzel et al., 2014). The Ge content in sulphide minerals (sphalerite and wurtzite) in SHMS deposits is between 0.1 and 1000 ppm Ge, and the average Ge content is in the order of 10s of ppm (Frenzel et al., 2014). During zinc smelting, Ge is enriched in the oxidic residues, typically by a factor of 10 compared to the



**Fig. 3.** Indium grade (g/tonne) versus tonnage ( $10^6$  tonnes) for the main indium-bearing ore deposit types (modified from Schwarz-Schampera and Herzig, 2002). Deposit 1- Kidd Creek; 2- Brunswick No.12; 3 - Heath Steele; 4 - Neves-Corvo; 5 - Letneye; 6 - Komsomolskoye; 7 - Podolskoye; 8 - Sibaiskoye; 9 - Gaiskoye; 10 - Bakr-Tau; 11 - Maranda J; 12 - Lau Basin; 13 - TAG; 14 - Rammelsberg; 15 - Långban; 16 - Tosham; 17 - Omodani; 18 - W.Shropshire; 19 - Freiberg; 20 - Carguaicollu; 21 - Bolivar; 22 - Colquiri; 23 - Porco; 24 - Huari Huari; 25 - San Vicente; 26 - Potosi; 27 - Dulong; 28 - Morococha; 29 - Ashio; 30 - Akenobe; 31 - Ikuno; 32 - Dachang; 33 - Toyoha; 34 - Equity Silver; 35 - Kirki; 36 - Elacite/Asarel; 37 - Santa Rita; 38 - Bingham; 39 - Mount Pleasant; 40 - Baal Gammon; 41 - Cinovec; 42 - Ulsan; 43 - Cerro de Pasco.

original zinc concentrate (Dutrizac et al., 1996). In SEDEX, Ge content is typically 10-100 ppm, in MVT deposits, it is in the range of 100-1000 ppm, and in Kipushi-type deposits, Ge is 10-1000 ppm (Höll et al., 2007). Germanium can also be recovered from VHMS deposits, although they typically have low Ge concentrations (<100 ppm; e.g., Kuroko deposits, Japan).

Sphalerite in the Red Dog SEDEX deposit has an average Ge content of about 100 ppm (Kelley et al., 2004). The Trail smelter in Canada, which processes the zinc concentrates from Red Dog and Pend Oreille mines, produced about 40 tonnes of Ge in 2007 (Guberman, 2010). SEDEX deposits in China typically have much lower Ge content in sphalerite (<10 ppm; Ye et al., 2011). Indium concentrations in sphalerite from the sandstone-hosted Jinding deposit are slightly higher, with values ranging from 1.8 to 56.3 ppm (Ye et al., 2011).

Known MVT districts have higher Ge content in their zinc

concentrates than SEDEX deposits, but values are variable. In MVT deposits, Ge is usually substituted into the sphalerite and wurtzite structures, and discrete Ge mineral inclusions are usually absent. Sphalerite at the Tres Marias MVT deposit in Mexico has on average 1000 ppm Ge (Melcher and Buchholz, 2014). The MVT deposits of the Tri-State district in the United States have 60 to 400 ppm Ge in sphalerite concentrates (Bonnet et al., 2014); those of the Appalachian Basin have much lower Ge values (avg. 10 ppm). MVT deposits of the Bleiberg district in Austria have on average 300 ppm Ge and produced a total of 126 tonnes of Ge. Sphalerite from the Huize MVT deposit in China has up to 354 ppm Ge, and sphalerite from the Niujiaotang MVT deposit has up to 546 ppm Ge (Bernstein, 1985; Höll et al., 2007, Ye et al., 2011). In Canada, the Pine Point MVT deposit has up to 600 ppm Ge (avg. 78 ppm; Paradis, unpublished data). Similar values are

obtained from sphalerite of the southern Canadian Cordillera MVT deposits (Paradis, unpublished data). In these deposits, Ge shows a positive correlation with Fe, and locally with Ga. Kipushi-type Cu-Zn-Pb-Ag-Ge deposits (Kipushi, Tsumeb and Kabwe) have some of the highest concentrations of Ge (up to 1.5%), and are host to several Ge-bearing minerals (e.g., briartite, reniérite, and germanite). Sphalerite in these deposits is not the main carrier of Ge as it contains <100 ppm Ge (Höll et al., 2007). Germanium is mostly carried by Ge minerals (germanite, reniérite, and briartite), stannoidite, enargite, and tennantite-tetrahedrite (Höll et al., 2007), which occur in Cu-rich and Zn-Cu-(Pb) mixed ores. It is interesting to note that Ge-rich ores may also be rich in Ga. At Kipushi in Democratic Republic of the Congo (DRC), the Cu-rich and Zn-Cu-(Pb) ores contain Ge- and Ga-rich ore masses that have up to 1.5% Ge and 2.5% Ga (Kampunzu et al., 2009). At Tsumeb, germanite (rare and replaced by reniérite at Kipushi) is the most abundant Ge-bearing phase. The Pb-Zn-Cu ore contains 0.6-1230 ppm Ge and 19-1130 ppm Ga (Kampunzu et al., 2009).

## 6. Major gallium-bearing deposit types with focus on sediment-hosted Zn-Pb deposits

Gallium is primarily recovered as a by-product from the industrial processes during the manufacture of aluminium metal upon treatment of bauxite, and processing of sphalerite in zinc sulphide ores. In bauxite, Ga occurs in concentrations of <10-160 ppm (avg. 50 ppm; Dittrich et al., 2011). Gallium concentrations in sphalerite of certain MVT deposits can reach values of 0.01 to 0.1%, greater than from most other types of deposits, but Ga content in these deposits is commonly erratic. As mentioned above, Ga can reach high concentrations in Kipushi-type deposits.

## 7. Relationship between In, Ge and Ga concentrations in sphalerite

Trace element content of sphalerite was suspected to indicate deposit-type for more than 75 years (Ofte Dahl, 1940). At least theoretically, the distinction can be made between the trace element signature of sphalerite in VHMS, SEDEX, MVT, skarns, and epithermal veins. Typically, In content is elevated in higher temperature systems, such as VHMS deposits, and Ga and Ge contents are higher in lower-temperature ores, such as MVT deposits (Cook et al., 2009).

## 8. Conclusions

Indium, Ge and Ga are minor and trace elements in a variety of mineral deposit types, but they can reach economic concentrations in base-metal deposits. Indium is typically more abundant in higher temperature base-metal deposits (i.e., VHMS), whereas Ge and Ga are more abundant in lower-temperature ore deposit-types (i.e., SEDEX and MVT). The presence or absence of these elements can, to a large extent, be correlated with ore deposit-type.

Indium, Ge and Ga are essential for a variety of high-technology applications such as integrated circuits, optoelectronic devices,

fiber optics, thin-film coatings, and metal alloys, and the future demand for these metals will continue to increase. Exploration for base-metals has been highly cyclical in recent decades, but resurgence of global exploration for base-metal deposits will likely result in increased In, Ge, and Ga reserves. Assuming that the principle of supply and demand applies to In, Ga, and Ge, high demand for these elements may result in search and preferential development of base-metal deposits with economically recoverable concentrations of these elements.

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