



Indium in cassiterite and ores of tin deposits



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ABSTRACT

The results obtained with LA-ICP-MS by less abundant lighter ¹¹³In isotope and EPMA show that in cassiterite–quartz veins the indium contents do not exceed 160 ppm, while cassiterite from Sn–sulfide veins is characterized by higher indium contents from 40 to 485 ppm; sulfides of Sn–sulfide veins unlike sulfides of cassiterite–quartz veins also have the highest indium contents: Fe–sphalerite (100–25,000 ppm), chalcocopyrite (up to 1000 ppm), and stannite (up to 60,000 ppm). Indium contents in the Sn–sulfide ore of the Tigrinoe and Pravourmiiskoe deposits obtained using SR-XRF, ICP-MS and atomic absorption methods range from 10 to 433 ppm with average values of 56–65 ppm. Indium-rich Sn–sulfide mineralization in five large Sn–Ag ore districts of the Far East Russia (Khingansky, Badzhalsky, Komsomolsky, Arminsky, Kavalerovsky) provides the impetus for further exploration of deposits with Sn–sulfide mineralization as the most promising indium resources in Russia. Empirical observations from geology and geochronology of cassiterite–quartz and Sn–sulfide mineralization show that the combined contribution from granite and alkaline–subalkaline mafic sources and multistage ore-forming processes doubled indium resources of deposits being the main factors in the formation of high grade indium mineralization.

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1. Introduction

Indium is a rare element and trace component in the composition of the Earth's crust. World production of indium has steadily increased during the last 10 years, because of increased demand for application in electronics, ultra-high vacuum technique, solar power plants, semiconductor and other industries. In Russia, commercial grade indium is currently recovered as a by-product from Sn–massive sulfide deposits (Gaiskoe and Sibaiskoe deposits, Urals), which have indium contents of 10–25 g/t. The growing demand for indium requires the evaluation of In contents in other types of deposits in an effort to identify alternative resources. Known indium resources and contents in ore have been evaluated in many deposits around the world (Schwarz-Schampera and Herzig, 2002), but until now there are only few published data for deposits in Russia. Many Russian researchers have studied the composition of ores and indium-bearing minerals, as well as indium contents in the ores and magmatic rocks (Butova et al., 1998; Flerov, 1976; Flerov et al., 1971; Gamyranin and Kokin, 1991; Gavrilenko and Pogrebs, 1992; Genkin and Muravjova, 1963; Indolev and Nevoisa, 1974; Ivanov and Rozbianskaya, 1961; Ivanov et al., 1963; Kiselev, 1948; Komarova and Novorossova, 1959; Nekrasov, 1966; Nikulin, 1967; Orlova, 1956; Pavlovskiy et al., 1977; Prokin and Buslaev, 1999; Semenyak et al., 1994; Zabarina et al., 1961).

There are indium minerals (indite FeIn_2S_4 , roquesite CuInS_2 and laforetite AgInS_2) and In-containing mineral-carriers in the ore veins of tin deposits. Indite replaced by dzhalindite $\text{In}(\text{OH})_3$ was found in fissures in cassiterite of cassiterite–quartz veins and in quartz veinlets intersecting quartz–cassiterite aggregate (Dzhalinda deposit, Khingansky ore district, Sikhote-Alin) (Genkin and Muravjova, 1963). In addition, there are micro-inclusions of stannite in cassiterite crystals (Fig. 1A) and veinlets with quartz, hydromica, In-bearing stannite and Fe–sphalerite in cassiterite aggregate (Fig. 1B, C), so reported high indium contents in cassiterite according to quantitative spectral analysis must be taken with a large degree of caution. Roquesite occurs usually in association with chalcocopyrite in Sn–sulfide and VMS deposits, laforetite is usually deposited in the composition of Sn–sulfide ore with galena and sphalerite, and in Sn–Ag carbonate veins at the periphery of Sn–Ag ore districts. In the oxidation zone indium enters the composition of supergene mineral yononamite. However, whole indium, which has been recovered during processing of the ores of hydrothermal tin and Sn-bearing VMS deposits, occurs as impurity in the In-bearing sulfides and sulfosalts. In recent years new data on the In contents in the mineral-carriers has been obtained (Cook et al., 2009, 2011a, 2011b, 2011c; Gavrilenko and Pogrebs, 1992; Jovic et al., 2011; Jung and Seifert, 1996; Kieft and Damman, 1990; Kissin and Owens, 1989; Moura et al., 2007; Murakami and Ishihara, 2013; Murao et al., 2008; Ohta, 1989; Seifert, 1994; Seifert and Sandmann, 2006; Semenyak et al.,

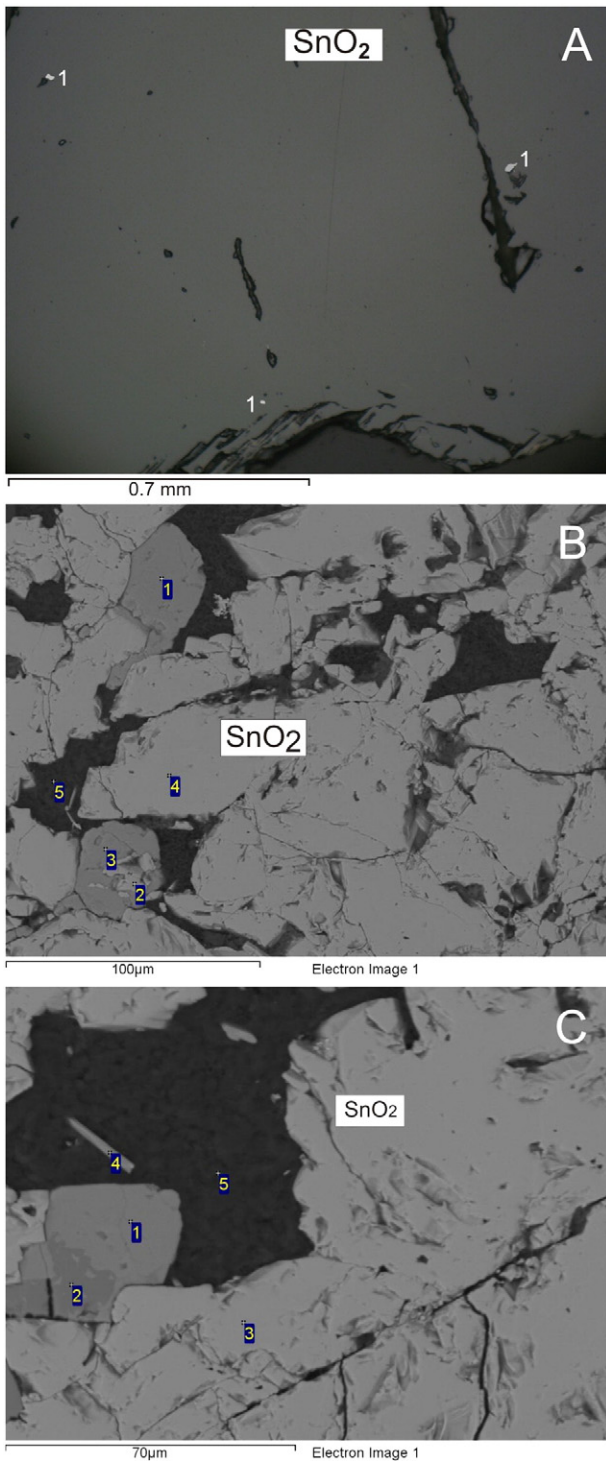


Fig. 1. Stannite in cassiterite crystal and aggregate: A – photomicrograph of stannite micro-inclusions (≤ 0.03 wt.% In, Table 2) in cassiterite crystal, quartz–cassiterite vein, Khrustalnoe deposit, Far East Russia. B – SEM image of cassiterite cut by veinlet with 1 and 3 – stannite (0.14 and 0.24 wt.% In, Table 3), 2 and 4 – cassiterite, 5 – hydromica. C – SEM image of veinlet in cassiterite with 1 – stannite (0.22 wt.% In, Table 3), 2 – Fe-sphalerite, 3 – cassiterite, 4 – tantalite–columbite, 5 – hydromica.

1994; Shimizu et al., 1986; Sinclair et al., 2006; Ye et al., 2011): Fe-sphalerite (0.1–7, rarely up to 13.5 wt.%), chalcopyrite (up to 0.1 wt.%), bornite (up to 0.4 wt.%), stannite and k esterite (≤ 3 wt.%), stannoidite (~ 0.1 wt.%), petrukite (0.7–6 wt.%), and sakuraiite (up to 17–23 wt.%).

It has been known that sulfide and sulphosalt minerals in some tin and VMS deposits contain modest amounts of indium, but the question

of whether indium can also be hosted in cassiterite remains poorly constrained. Common methods for determining the indium content in cassiterite include electron probe microanalysis (EPMA), wet chemical or spectral analysis but these methods do not provide satisfactory answers to the question. The disadvantage of EPMA is that the minimum detection limit of analysis (± 0.06 wt.%) may exceed the actual In content in the mineral. In addition, analytical precision may be low because of superposition of the Sn and In analytical lines. The disadvantages of wet chemical and spectral analysis include the fact that, firstly, cassiterite often contains mineral micro-inclusions (indite, stannite) which contain indium as main components (up to a few wt %). It is therefore possible to overestimate the results obtained from samples containing such micro-inclusions. Second, wet chemical and spectral analyses also have minimum detection limits that do not permit detection of In contents below 10 ppm (0.001 wt.%).

2. Samples and deposits

Sample material was selected from tin deposits of the Far East Russia and Northern Vietnam, Yakutia, Kyrgyzstan (Tian-Shan), Tadjikistan (Pamir), Germany (Erzgebirge), and the only Sn deposit in Tuva (Russia) (Appendix A). Cassiterite samples are selected from cassiterite–quartz veins of the Deputatskoe large tin deposit in Yakutia, Trudovoe (Tian-Shan), Trezubetz and Kobrigen (Pamir) Sn deposits, from cassiterite–quartz and cassiterite–sulfide veins of tin deposits in Vietnam and Tuva by authors during field works.

Cassiterite from cassiterite–quartz and cassiterite–sulfide veins of several tin deposits of the Far East Russia including Silinskoe, Khrustalnoe (Kavalerovskiy ore district, Sikhote-Alin), Valkumey, Pervonachalnoe (Chukotka), Pridorozhnoe and Solnechnoe (Komsomolsky ore district, Sikhote-Alin) are selected from the vein samples in mineral collections of the Institute of Geology and Mineralogy SB RAS. Sulfides are taken from cassiterite–sulfide veins of the Tigrinoe, Khrustalnoe, Pridorozhnoe (Far East Russia), and Tashkoro (Kyrgyzstan) deposits. Samples from the Tigrinoe deposit are taken from the mine and represented by cassiterite–quartz veins with muscovite, cassiterite–quartz greisen and sphalerite ore veins from quartz–topaz–cassiterite–sulfide veins in different proportions. Ore samples of the Pravourmiiskoe deposit are taken from the adit and consist of predominating sulfides: chalcopyrite, sphalerite and arsenopyrite (from 15 to 50%) with cassiterite (5%), quartz and topaz (from 15 to 50%), tourmaline (up to 10%), and bornite (up to 25% in 118–87 sample), \pm rare fluorite, wolframite.

Tailings of cassiterite taken from the Novosibirsk tin plant consist of uniform mixture of fine mineral particles which range from sand-type grain size to a few micrometers, in some samples ore minerals are completely oxidized (samples Sn-z 1–3), whereas others are weakly oxidized sulfides. Average chemical composition of tailings (wt.%): SiO₂ 28.9, Al₂O₃ 7.3, CaO 5.6, Sn 1.8, WO₃ 0.13, Zn 0.5, Cu 0.6, Pb 0.7, Fe 16.1, As 2.6, S 3.3, Sb 0.01. Tailings were analyzed for purposes of comparison.

2.1. Deposits

Cretaceous tin mineralization in Pamir is represented by simple cassiterite–quartz veins and greisen at the Trezubetz and Kobrigen deposits (97.5 ± 1.0 – 98.2 ± 1.0 Ma, $^{40}\text{Ar}/^{39}\text{Ar}$, muscovite) localized in Carboniferous, Permian and Triassic terrigenous-carbonate rocks and linked with adamellite, granite, leucogranite and ongonite dikes 100.5 ± 1.8 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$, zinnwaldite) of the Bazardara complex (Pavlova et al., 2010).

The Deputatskoe is highest grade tin deposit in Yakutia. The Sn–Ag Deputatsky ore district is located in Jurassic flysch sediments intruded by hidden granitic pluton with accompanying greisen (112 Ma). Multi-stage mineralization consists of: 1) greisen-1 and cassiterite–quartz veins, 2) cassiterite–tourmaline–sulfide, and 3) low-temperature carbonate veins with siderite, galena, sphalerite and Ag–Pb–Sb sulfosalts.

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