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Book Title	XIII General Meeting of the Russian Mineralogical Society and the Fedorov Session	
Series Title		
Chapter Title	Sulfostannates of Zwitter-Tourmalinite Complexes Accompanying the Lithium-Fluoric Granites (On the Example of Pravouriysky Rare-Metal-Tin Deposit)	
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Sulfostannates of Zwitter-Tourmalinite Complexes Accompanying the Lithium-Fluoric Granites (On the Example of Pravourmiysky Rare-Metal-Tin Deposit)

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Abstract. The complex of sulfostannates from the Pravourmiyskoye greisen deposit in the Far East of Russia is discussed. The complex includes stannoidite, mawsonite, stannite, sakuraiite. The discovery and typomorphic features of ferrokësterite and kësterite are noted. Zwitter-tourmalinite metasomatic complexes accompanying the lithium-fluoric granites are distinguished by high ore fertility and lithochalcophilic specialization. They combine cassiterite, wolframite, sulfides (arsenopyrite, lollingite, chalcopyrite, bornite, sphalerite, pyrrhotine, bis-muthinite, etc.) and sulfostannates with an admixture of In, Ag, Cd. It is proposed to use sulfostannates as minerals indicating large-scale formation of rare-metal-tin ore.

Keywords: Sulfostannates · Kësterite · Ferrokësterite · Stannoidite · Mawsonite · Stannite · Zwitter · Greisen deposits · Lithium-fluoric granites · Pravourmiyskoye deposit · Amur River region

1 Introduction

In prospecting mineralogy, particular attention is given to rare minerals and mineral parageneses, formed in abnormal geochemical environment and capable of serving as indicators of ore-rich large and unique deposits (Gavrilenko et al. 2000). Greisen deposits associated with leucogranites are mainly characterized by lithophilic geochemical specialization (Si, Al, F, Sn, W, Mo, Be, Rb, Li, etc.). The appearance of chalcophilic quartz-sulfide mineralization in them (Cu, Zn, Pb) is connected with late stages of hydrothermal processes (Plyushchev et al. 2012). Among greisen formations, zwitter-tourmalinite metasomatic complexes (ZTC) related to lithium-fluoric granites clearly stand out by their composition and high ore fertility (Alekseev 2014).

In 1948, A.I. Kiselev found stannite enriched with zinc and silver in the topaz-containing greisens of the Këster deposit in Yakutia (Kiselev 1948). Soon it was called “kësterite” and approved by the CNMMN IMA as a new mineral (Orlova 1956; Bonstedt-Kupletskaya 1958). A little later, a ferri-ferrous analogue of kësterite – ferrokësterite was

described in Cornwall greisens of Great Britain (Kissin and Owens 1989). Bibliometric data from Web of Science show a rapid increase in the number of publications devoted to k  sterite and ferrok  sterite: 18 to 2000, 69 during the period 2000–2010 and 1785 over the past ten years. Such a high interest in a rare minerals is caused by its semiconductor properties: laboratories in many countries are intensively developing technologies for the use of synthetic k  sterite as a cheap and environmentally friendly substitute for tellurides, arsenides and selenides of Cd, In, Ga, traditionally used in the production of solar cell battery (Wallace et al. 2017; Dhawale et al. 2019).

2 Materials and Methods

Mineral associations of the ZTC were investigated on the example of a large Pravourmiyskoye rare-metal-tin deposit associated with the eponymous complex of lithium-fluoric granites in the Badjal ore district (Amur River region) and of the K  ster rare-metal-tin deposit associated with the eponymous complex of lithium-fluoric granites in the Yano-Adychansky ore district (Yakutia). At the Pravourmiyskoye deposit in the crossdrift No. 568 of day-hole No. 5, 5 quartz-topaz veins with wolframite, cassiterite and sulfides were collected samples. In the bore specimen of drill hole No. 37 and 38, which opened the K  ster deposit of topaz-lepidolite-muscovite greisens with cassiterite, 3 samples of quartz veins with cassiterite and sulfides were taken.

Ore petrography of the 8 samples using reflected and transmitted light was carried out using an Leica DM2500 M microscope. Ore textures were assessed and representative samples were examined further by SEM-EDS methods. The internal structure, composition and relationship of sulphides were investigated in polished section using a JEOL JSM-6460LV equipped with an Oxford Instruments INCA EDS system in the Microanalytical Centre at St. Petersburg Mining University. Survey conditions: COMPO imaging signal, accelerating voltage 20 kV, beam current 1.5 nA.

The composition of k  sterite and ferrok  sterite was investigated in the same Centre using a JEOL JXA-8230 with four WDS spectrometers and PETJ, LIF crystals. The analyses were performed using a beam current of ~20 nA, accelerating voltage of 20 kV, probe diameter 1 μm , and live times of 30 s. ZAF corrections were used for the correction procedure. The standards used were pyrite ($\text{FeK}\alpha$, $\text{SK}\alpha$), sphalerite ($\text{ZnK}\alpha$), chalcopyrite ($\text{CuK}\alpha$), InAs ($\text{InL}\alpha$), Sn ($\text{SnL}\alpha$), Ag ($\text{AgL}\alpha$). The number of EPMA analyses of ferrok  sterite is 16, k  sterite is 7. To distinguish the minerals of the stannite group, the stoichiometric criteria proposed were used in (Kissin and Owens 1989). When studying the structure and relationships of k  sterite-ferrok  sterite and associating sulfides, the concept of minerals ontogeny was used (Alekseev 2014; Brodskaya and Marin 2016).

3 Results

Due to the enough study of the k  sterite deposit (Kiselev 1948; Bonstedt-Kupletskaya, 1958; Kokunin 2011) below is described only ferrok  sterite of the Pravourmiyskoye deposit. This deposit is the richest source of tin (more than 100 thousand tons) and associated rare and basic metals: tungsten, copper, bismuth, niobium, indium, scandium. The expedition of the Saint-Petersburg Mining University organized under the direction

of Yu.B. Marin in the ZTC of the Pravourmiyskoye deposit established an association of sulfostannates - stannoidite, mawsonite, stannite (Gulbin and Evangulova 1987). For the first time sakuraiite and k  sterite were identified in zwitter (Alekseev 2014) (Table 1). In the composition of sulfostannates, variable concentrations of impurities, represented by In, Ag, Cd, were recorded.

Rich sulphide mineralization was determined on the eastern flank of Pravourmiyskoye deposit. In the axial part of the zwitter zone are concentrated steeply pitching cassiterite-topaz veins with a thickness of 3–16 cm. They intersect with quartz-tourmaline veinlets (0.5–4 cm). Veins contain cassiterite, wolframite and up to 3–15% of sulfides, among which prevail arsenopyrite, chalcopyrite, sphalerite, pyrrhotine, galenite prevail. Sulfides are distributed in veins and near-lying greisens in form of dissemination, veinlets and polymineral bonny measuring 1–12 cm (Fig. 1).

In topaz veins, for the first time was found ferrok  sterite, represented by isometric and lenticular secretions 5–20   m across, located in the marginal parts of the aggregates of pyrrhotine and high-iron sphalerite (Fe/Zn 0.20–0.29), on the border with quartz, topaz and fluorite (Fig. 2). The internal structure of ferrok  sterite is uniform. No mineral inclusions larger than 6 nm were detected. Ferrok  sterite stoichiometrically corresponds to standards from the Kliga deposit in Cornwall (Kissin and Owens 1989) and Mount Pleasant in Canada (Sinclair et al. 2006). The empirical formula of the mineral: $\text{Cu}_{1.89}(\text{Fe}_{0.97}\text{Zn}_{0.13})\text{Sn}_{0.99}\text{S}_{4.01}$. Signs of ferrok  sterite of the Far East: excessive iron content ($\text{Fe}/(\text{Fe} + \text{Zn}) = 0.73 \div 0.92$) and deficiency of copper, indium and silver, as well as other rare elements (Cd, Bi, As, Se), characteristic of its analogues from the tin ore deposits around the world.

Table 1. Mineral associations of zwitter-tourmalinite complex from the Pravourmiyskoye deposit

Mineral association	Minerals of zwitter	Minerals of tourmalinites
Sulfostannates of Cu, Fe, Zn, In	Ferrok��sterite, sakuraiite	Stannoidite, stannite, mawsonite
Sulphides of Cu, Fe, As, Zn, Bi, In	Arsenopyrite 1, lollingite, bismuthinite, sinnerite, sphalerite 1, pyrrhotine	Chalcopyrite, bornite, sphalerite 2, roquesite и др
Rare metal minerals	Cassiterite, wolframite, monazite, xenotime, fergusonite, pyrochlore и др	Cassiterite, monazite, Ce-epidote

4 Discussion

The finding of ferrok  sterite on eastern flank of the Pravourmiyskoye deposit is not accidental. It is connected with the inclination of ore bodies to the east and a decrease in their erosion cut in this direction. Ferrok  sterite was found on the uppermost tier of a greisen-ore column enriched with base metals, and on the eastern flank of the ore zone

it replaces stannoidite and stannite as part of sulfostannates. It replaces stannoidite and stannite on eastern flank of the ore zone as part of sulfostannates. Replacement of stannite to ferrokësterite according to the scheme: $\text{Cu}_2\text{FeSnS}_4 + \text{ZnS} \rightarrow \text{Cu}_2(\text{Fe}, \text{Zn})\text{SnS}_4 + (\text{ZnFe})\text{S}$ (Osadchii and Sorokin 1989). At the Këster deposit, kësterite is also confined to upper part of the greisens ore delf. It displaces the stannite as part of the sulfide complex, and associated with cassiterite, sphalerite, pyrrhotine and arsenopyrite (Kokunin 2011).

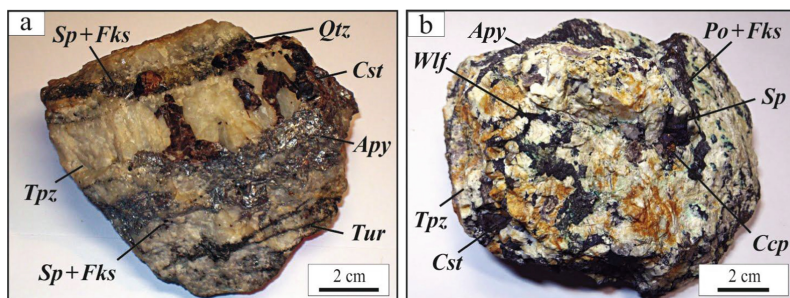


Fig. 1. Topaz veins with cassiterite, wolframite, sulfides, and ferrokësterite from zwitter of the Pravourmiyskoye deposit: a – topaz vein with cassiterite, arsenopyrite, with bonny of sphalerite and ferrokësterite; b – topaz vein with cassiterite, wolframite, arsenopyrite, chalcopyrite, with bonny of sphalerite, pyrrhotine and ferrokësterite. Apy – arsenopyrite, Ccp – халькопирит, Cst – cassiterite, Fks – ferrokësterite, Po – pyrrhotine, Sp – sphalerite, Tpz – topaz, Tur – tourmaline, Qtz – quartz, Wlf – wolframite.

Greisen deposits associated with leucogranites are mainly characterized by lithophilic geochemical specialization (Si, Al, F, Sn, W, Mo, Be, Rb, Li, etc.). ZTC of large rare-metal-tin ore deposits accompanying the lithium-fluoric granites (Ehrenfriedersdorf, Germany; Baga-Ghazryn, Mongolia; Mount Pleasant, Canada; Lost River, Alaska; Odnokoe, Yakutia; Tigrinoe, Primorye, etc.), are characterized by specific mixed mineral paragenesis (Alekseev 2014). On the one hand, they are composed of lithophilic minerals (quartz, light mica, topaz, albite, etc.) and contain accessory and ore mineralization typical of rare-metal-tin ore deposits (cassiterite, wolframite, beryl, fluorite, tantalum-niobates, etc.). On the other hand, they are saturated with chalcophilic rock-forming and ore minerals – zinnwaldite, tourmaline and sulfides – arsenopyrite, chalcopyrite, sphalerite, etc. Emblematic for the mineralogy of ZTC is the presence of complex sulfides – sulfostannates: stannite, stannoidite, kësterite, etc. (Parrish 1977; Kissin and Owens 1989; Sinclair et al. 2006; Moura et al. 2007; Kokunin 2011; Popova et al. 2013; Alekseev 2014; Wu et al. 2017).

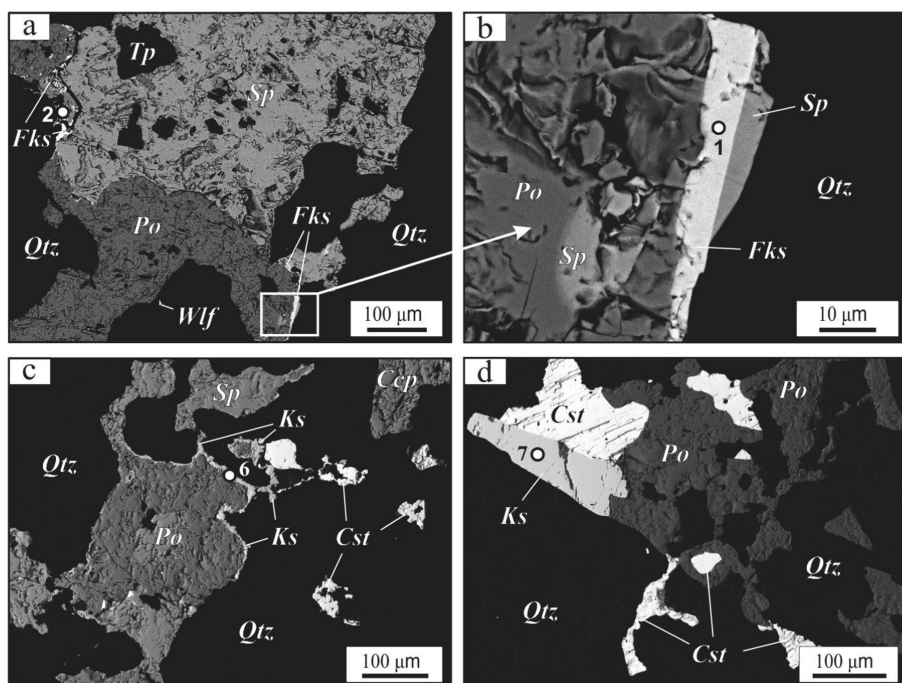


Fig. 2. Ferrokësterite and kësterite in greisen associated with Li-F granites of the Pravourmiyskoye (a, b) and Kester (c, d) deposits: a – ferrokësterite in the place of contact with pyrrhotine and high-iron sphalerite; b – fragment of Fig. 2, a: ferrokësterite vein; c – encrustation of pyrrhotine with kësterite in the place of contact with cassiterite and sphalerite in quartz veins; d – aggregate of kësterite with cassiterite and pyrrhotine in a cassiterite-quartz vein. Ccp – chalcopyrite, Cst – cassiterite, Fks – ferrokësterite, Gn – galena, Ks – kësterite, Po – pyrrhotine, Sp – sphalerite, Tp – topaz, Qtz – quartz, Wlf – wolframite.

Sulfostannates are attributed of silicate-sulfide tin-polymetallic ore deposits. Their emergence in association with rare-metal minerals of the cassiterite-quartz formation can be explained by an increased concentration of copper and sulfur at the final stages of greisenization process. As reducing conditions are established, sulfostannates are successively formed: sakuraiite → ferrokësterite → stannite → stannoidite → mawsonite.

The list of kësterite finds in greisen deposits in the Far East of Russia, Canada with high-temperature paragenesis of topaz, cassiterite, arsenopyrite, wolframite, kësterite and cubic stannite is expanding (Bonstedt-Kupletskaya 1958; Parrish 1977; Cerny and Harris 1978; Kokunin 2011; Popova et al. 2013). Ferrokësterite is also discover in relatively high-temperature deposits in South America, Canada, Great Britain, combining greisen-arsenopyrite and hydrothermal base metal-sulfide mineralization (Kissin and Owens 1989; Betterton et al. 1998; Sinclair et al. 2006; Torres et al. 2019).

From the geodynamics viewpoint the considered greisen-magmatic systems (Yano-Adychan district in Yakutia, Badjal district in the Amur river region, Arminsky district in Primorye, Cornwall in the UK, Mount Pleasant in Canada, etc.), are formed along

the boundaries of stable geoblocks, in the inner region of continental margin. It is recommended to consider sulfostannates as mineral indicating large-scale formation of rare-metal-tin ore.

A great practical interest to k sterite is related to its semiconductor properties, making it a promising multicomponent material for solar energy conversion (Wallace et al. 2017; Dhawale et al. 2019). Given the high prospects for application of synthetic k sterite for the production of solar panels, ferrok sterite should be investigated as a likely natural prototype of a new optoelectronic material for converting solar energy into electricity.

5 Conclusions

Thus, the zwitter-tourmalinite complexes accompanying the Li-F granites is characterized by a mixed lithochalcophilic specialization of ores. The presence, species diversity and variable composition of sulfostannates in greisens (ferrok sterite, sakuraiite) and tourmalinites (stannoidite, stannite, mawsonite) have been established. You can conclude about the mineralogical features of large oregenesis of the Pravourmiyskoye deposit and extrapolate this conclusion to rare-metal-tin deposits associated with lithium-fluoride granites.

Ferrok sterite is a likely natural prototype of a new optoelectronic material for converting solar energy into electricity.

Acknowledgments. The reported study was funded by RFBR, project number 20-15-50064.

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Chapter 18

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