LA-ICP-MS STUDY OF TRACE ELEMENTS IN SPHALERITE AND CHALCOPYRITE FROM THE GIERCZYN MINE, POLAND

Krzysztof FOLTYN[1], Adam PIESTRZYŃSKI[1], Viktor BERTRANDSSON ERLANDSSON[2], Frank MELCHER[2]

[1]*AGH University of Science and Technology, Faculty of Geology Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Krakow, Poland; kfoltyn@agh.edu.pl*
[2]*Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria*

Introduction

The Karkonosze–Izera Massif (KIM) is a tectonic unit in the West Sudetes on the NE margin of the Bohemian Massif, located in Poland and Czech Republic. The KIM consist of the Karkonosze Granite intrusion and its metamorphic envelope. The northern part of the metamorphic envelope, Izera Gneisses, contains three schist belts: the northern Złotniki Lubańskie, the central Stara Kamienica and the southern Szklarska Poręba. They are composed mainly of mica schists and were metamorphosed under the conditions of upper greenschist and lower amphibolite facies.
Low-grade tin deposit in the Stara Kamienica Schist Belt is accompanied by polymetallic sulfide/sulfosalt assemblage and form a stratabound body in the middle part of a chlorite–mica–quartz schist suite rich in garnets. Extensive description of ore minerals from this locality has been done by Mochnacka and Piestrzyński (2003) and Michniewicz (2003). The ore assemblage in general consist of many different sulfides, arsenates and sulfosalts with pyrrhotite and chalcopyrite being the most abundant ones. The origin of this tin deposit is still a matter of discussion and there are several models for its formation. Hydrothermal origin is generally accepted but some authors attribute it to the Ordovician, granitic protolith of the Izera Gneisses while others to the Variscan Karkonosze Granite (see Michniewicz 2003, Mochnacka et al. 2015). Several investigations (e.g. Piestrzyński and Mochnacka 2003) reported indium admixtures in cassiterite and sphalerite while slight indium enrichment has also been noted in the whole rock samples (Mikulski et al. 2018). Mikulski et al. (2018) reported that sakuraiite – $(Cu,Zn,Fe)_3(In,Sn)S_4$ is the carrier of indium.
Progress in the laser ablation inductively-coupled mass spectrometry (LA-ICP-MS), gives an opportunity to precisely measure trace element content in base metal sulphides. Of special importance is recent development of matrix-matches sphalerite reference material MUL-ZnS 1 (Onuk et al. 2017) which improves accuracy and precision of the analyses.

Samples and methods

5 archival samples, collected by prof. Ksenia Mochnacka in the closed Gierczyn mine, containing macroscopically visible sphalerite and chalcopyrite, has been selected for LA-ICP-MS study. Trace element analyses were carried out at the Department of Applied Geosciences and Geophysics, Montanuniversität Leoben, Austria, using an ESI NWR213 Nd:YAG laser ablation system coupled to an Agilent 8800® triple quadrupole ICP-MS. Helium was used as carrier gas with a flow rate of 0.75 L/min. Fluency was set between 2-3 J/cm^2. For sphalerite and chalcopyrite analyses, the matrix-matched sintered pressed powder pellet reference material MUL-ZnS 1 (Onuk et al. 2017) was used for quantification of the element content and the USGS powder pressed polysulfide reference material MASS-1 was used for quality control of the analyses. Data reduction was done using the Iolite V3.1 software. The following isotopes have been analyzed: ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{71}Ga, ^{74}Ge, ^{75}As, ^{82}Se, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{201}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi.

Results and conclusions

Results of the investigation has been summarized in the Tab. 1. The most abundant trace elements in sphalerite are iron (ca. 10%) and cadmium (ca. 0,4%). Low concentrations of arsenic and germanium together with enrichment in cobalt (182-225 μg/g) have been measured, which show similarities with samples from skarn deposits (Frenzel et al. 2016). GGIMFis geothermometer gave temperatures in the range of 331-349°C which probably reflect closure of the sphalerite system at around ~310 °C during retrograde metamorphism (Frenzel et al. 2016).

Table 1. *The results of LA-ICP-MS measurments in µg/g.*

	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Ag	Cd	In	Sn	Sb	Pb	Bi
Chalcopyrite																	
MEDIAN (11)	10.3	-	9.9	2	-	626	2.7	0.3	0.4	67	144	4.7	99	420	2.3	3.6	2.2
MIN	10	-	3.3	1.6	-	499	0.3	0.2	-	43	129	0.9	67	226	0.1	0.4	0.2
MAX	10.8	-	11.6	4.4	-	751	3.5	0.5	0.8	82	149	5.3	117	663	7	16	8.7
Sphalerite																	
MEDIAN (22)	87	101 098	195	0.2	677	-	3.8	0.3	0.6	65	1.7	4 168	359	1.6	0.3	0.6	0.5
MIN	70	85 302	182	<0.1	301	-	2.9	0.1	<0.1	45.5	0.7	3 945	347	0.4	<0.1	<0.1	<0.1
MAX	139	118 023	225	4.4	6 894	-	4.6	0.5	1.2	77	7.6	5 405	433	11.7	47.4	59	7.9

Analyses confirmed that sphalerite hosts indium (up to 433 µg/g) but also show that chalcopyrite contains increased concentrations of this element (up to 117 µg/g). This results indicate that also chalcopyrite is an important host of indium, especially when we take into account that it’s more abundant than sphalerite in the deposit. Chalcopyrite contains over 100 µg/g of Zn, Ag and Sn and trace elements content in general slightly resembles the values reported from the Baita Bihor skarn deposit in Romania (George et al. 2018).

Co-genetic sphalerite and chalcopyrite both contains Ga at single µg/g level. George et al. (2016) and George et al. (2018) investigated hydrothermal chalcopyrite and partitioning of elements between co-crystallizing phases to conclude that under metamorphic conditions of amphibolite facies or above, both Ga and Sn will tend to partition into chalcopyrite over co-crystallizing sphalerite, distinct from the preferred host of these trace elements at lower temperatures. In recrystallized deposits, chalcopyrite will also typically host more Sn than co-crystallizing sphalerite or galena. Our results, especially the content of gallium, indicate that sulphides from the Gierczyn mine could have recrystallized during the metamorphism. It supports the observations of Michniewicz (2003) that both tin and slightly later sulphides mineralisation are pre-metamorphic and as a result cannot be related to the Variscan Karkonosze Granite intrusion.

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