# Minor and trace elements in sphalerite from lead-zinc-ores in the Ötztal-Stubai complex

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# Introduction

In this abstract we present preliminary results of a regional study on the distribution of minor and trace metal in Pb-Zn ores from the metamorphic units of the Ötztal-Stubai complex (ÖSC). The aim of the survey is to evaluate the economic potentials and understand the fundamental enrichment processes of High-Tech metals, such as gallium, germanium, indium, tin, antimony, and deleterious metals cadmium and mercury in metamorphosed sulphide ore. The sample set derives from the old mining districts Tösens and Nauders in the western part, and Schneeberg in the eastern part of the ÖSC. The chemical data presented here are from 423 laser ablation ICP-MS spot analyses.

The polymetallic ore district ÖSC includes numerous occurrences of stratiform sulphide mineralisations hosted in paragneisses. The two main, regionally distinct, metal associations are the northern Cu-Fe dominated association with chalcopyrite-pyrite-pyrrhotite±arsenopyrite± sphalerite parageneses and the southern Pb-Zn dominated association with sphalerite-galena±chalcopyrite±pyrite-pyrrhotite parageneses (VAVTAR, 1988). Despite abundant presence of mobilised sulphide-rich veins, the overall lithostratigraphic context suggests an early Palaeozoic, clastic dominated sedimentary exhalative (CD-SEDEX) genesis. Ordovician, Variscian and Eoalpine Orogenies led to a variable and polyphase, metamorphic overprint (low- to high-grade, local high-pressure).

## Petrography

Following textures of sphalerite are categorised: (1) massive vein sphalerite, (2) pegmatoidal vein sphalerite, (3) disseminated sphalerite (coarse patches, fine homogeneous, or between mica), (4) cataclastic sphalerite, and (5) sphalerite breccia cement. The most common sulphides associated with sphalerite are galena, chalcopyrite, pyrite and pyrrhotite, which local occurrences of arsenopyrite, tetrahedrite, boulangerite and gudmundite. Compositional zoning in sphalerite is commonly absent, although there are local crystallographically controlled variation in Fe and Zn. Microinclusions in sphalerite are heterogeneously distributed within the sample set, and commonly include chalcopyrite, galena or Fe-sulphides (pyrite or pyrrhotite).

# Trace element data

Following isotopes of minor and trace elements were monitored: <sup>34</sup>S, <sup>51</sup>V, <sup>52</sup>Cr, <sup>55</sup>Mn, <sup>56</sup>Fe, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>66</sup>Zn, <sup>71</sup>Ga, <sup>74</sup>Ge, <sup>75</sup>As, <sup>82</sup>Se, <sup>95</sup>Mo, <sup>107</sup>Ag, <sup>111</sup>Cd, <sup>115</sup>In, <sup>118</sup>Sn, <sup>121</sup>Sb, <sup>205</sup>Tl, <sup>208</sup>Pb and <sup>209</sup>Bi. Analytical protocol and calibration were performed following ONUK et al. (2016).

In terms of minor elements (i.e., > 0.1 wt%), all analysed sphalerites have Fe and Cd concentrations ranging from ~3 to ~9 and ~0.1 to ~0.5 wt%, with highest values exhibited in the Schneeberg samples. Other deposits show Fe concentrations < 7 wt%, although micro-pyrite/pyrrhotite inclusions in two samples from Knappenkar and Sattelalpe lead to abnormally high Fe contents (> 8 wt%). Following deposit averages for trace elements (in order of atomic number) are exhibited: Cr: 0.5 to 0.8 ppm, Mn: 13 to 380 ppm, Co: 0.2 to 454 ppm (highest in Tösens), Ni: 0.2 to 15 ppm, Cu: 180 to 3,790 ppm, Ga: 0.8 to 780 ppm (highest in Hochjoch), Ge: 0.1 to 138 ppm (highest in Tösens-Unterbergler Gang and Tscheyjoch), As: 0.1 to 63 ppm, Se: 11 to 17 ppm, Ag: 4.2 to 128 ppm (highest in Sudleskopf), In: 0.3 to 254 ppm (highest in Knappenkar), Sn: 0.2 to 187 ppm (highest in Tösens-Oberbergler Gang and Sudleskopf), Sb: 2.2 to 282 ppm (highest in Sudleskopf and Tscheyjoch), Hg: 16.5 to 397 ppm (highest in Schneeberg), Pb: 25 to 2,264 ppm, Bi: below de-

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Text-Fig. 1.

Box-and-whisker plots of Ga+Ge+Co+In+Sn in sphalerite for all studied deposits and occurrences in the ÖSC. On the right side values for metamorphosed SEDEX and VHMS deposits in Norway and Australia are shown (LOCKINGTON et al., 2014).

tection to 7 ppm (highest in Tösens). Extremely high (< 1,000 ppm) Cu and Pb concentrations are attributed to chalcopyrite and galena "diseases".

## **Discussion and conclusions**

The quantified trace metals are either located in the sphalerite lattice as defects substituting Zn on its IV-coordinated position, or they are hosted in microscopic solid inclusions. In general, the distribution of trace metals in sphalerite is controlled by several, competing or enhancing, geochemical factors: (a) availability of the element in relation with Zn, (b) crystal-chemical compatibility in the IV-coordinated position of the cubic lattice, (c) competition between co-precipitated phases. These factors were active during mineralisation and subsequent phases of remobilisation and recrystallisation.

The high Fe and Cd concentration in Schneeberg samples are primarily related to a higher eoalpidic metamorphic grade in the eastern part of the ÖSC. The Hg concentrations show remarkably low standard deviations within samples and its covariance with Cd suggests that this element is located within the sphalerite lattice. The distinct Hg and Mn variations amongst the deposits allow to a discrimination based on these elements. There is a low-Mn/high-Hg (Tösens, Nauders/Tscheyjoch) and a high-Mn/low-Hg (Nauders/Knappental, Nauders/Knappenkar, Sattelalpe) subgroup. Schneeberg shows untypically variable Hg, suggesting that the Hg chemistry may be zoned across this complex deposit. More investigations of controlling factors for metal distribution will follow.

In terms of total sphalerite-hosted "critical metal" (Ga+Ge+Co+In+Sn) abundance, the comparison with metamorphosed massive base metal deposits in Norway and Australia (LOCKINGTON et al., 2014) reveals that the occurrences in the ÖSC can compete with others (Text-Fig. 1). The Tösens deposit shows highest mean and median Ga+Ge+Co+In+Sn sums in the data set including ÖSC, Norwegian and Australian values.

#### References

- LOCKINGTON, J.A., COOK, N.J. & CIOBANU, C.L. (2014): Trace and minor elements in sphalerite from metamorphosed sulphide deposits. – Mineralogy and Petrology, **108**, 873–890, Wien.
- ONUK, P., MELCHER, F., MERTZ-KRAUS, R., GÄBLER, H.E. & GOLDMANN, S. (2016): Development of a Matrix-Matched Sphalerite Reference Material (MUL-ZnS-1) for Calibration of In Situ Trace Element Measurements by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. Geostandards and Geoanalytical Research, 10 p., online version, Vandoeuvre-lès-Nancy. DOI: https://dx.doi.org/10.1111/ggr.12154
- VAVTAR, F. (1988): Die Erzanreicherungen im Nordtiroler Stubai-, Ötztal- und Silvrettakristallin. – Archiv für Lagerstättenforschung der Geologischen Bundesanstalt, 9, 103–153, Wien.