



# Partitioning of trace elements in co-crystallized sphalerite–galena–chalcopyrite hydrothermal ores



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## ABSTRACT

There is an abundance of published trace element data for sphalerite, galena and chalcopyrite in natural systems, yet for a co-crystallized assemblage comprising these base metal sulphides, there is no detailed understanding of the preferred host of many trace elements. Laser-ablation inductively-coupled plasma mass spectrometry trace element maps and spot analyses were generated on 17 assemblages containing co-crystallized sphalerite and/or galena and/or chalcopyrite from 9 different ore deposits. These deposits are representative of different ore types, geologic environments and physiochemical conditions of ore formation, as well as superimposed syn-metamorphic remobilisation and recrystallization. The primary factors that control the preferred base metal sulphide host of Mn, Fe, Co, Cu, Zn, Ga, As, Se, Ag, Cd, In, Sb, Te, Tl and Bi are element oxidation state, ionic radius of the substituting element, element availability and the maximum trace element budget that a given sulphide mineral can accommodate. Temperature, pressure, redox conditions at time of crystallization and metal source, do not generally appear to influence the preferred base metal sulphide host of all the trace elements. Exceptions are Ga, In and Sn recrystallized at high metamorphic grades, when the preferred host of Ga and Sn usually becomes chalcopyrite. In more typical lower temperature ores, the preferred host of Ga is sphalerite. Indium concentrations also increase in chalcopyrite during recrystallization. At lower temperatures the partitioning behaviour of Sn remains poorly constrained and shows little predictable pattern among the data here. The results obtained may be used as a tool to assess co-crystallization. If trace element distributions in a given base metal sulphide assemblage match those reported here, and assuming those distributions have not been significantly altered post (re-) crystallization, then it may be suggestive of a co-crystallized assemblage. Such information provides a foundation for novel attempts to develop trace element-in-sulphide geothermometers.

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## 1. Introduction

Application of multi-element microanalytical techniques, e.g., micro-particle-induced X-ray emission ( $\mu$ -PIXE), secondary ion mass spectrometry (SIMS), electron probe microanalysis (EPMA), or laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), has become commonplace in many fields of geology, including studies relating to ore genesis. This is largely due to the accurate *in-situ* concentration data these techniques can generate, with both sub-part-per-million level precision (for  $\mu$ -PIXE, SIMS and LA-ICP-MS) and micrometre-scale spatial resolution. As a result, large amounts of trace element data have been published on many common ore minerals, including the base metal sulphides (BMS), sphalerite (ZnS), galena (PbS) and chalcopyrite ( $\text{CuFeS}_2$ ) (e.g., McIntyre et al., 1984; Cabri et al., 1985; Foord and Shawe, 1989; Cabri, 1992; Huston et al., 1995; Larocque et al., 1995; Moggi-Cecchi et al., 2002; Cook et al., 2009, 2011a; Lockington et al.,

2014; George et al., 2015). As such, the diversity of trace elements and ranges of concentration that these sulphides can incorporate has been relatively well documented. However, the partitioning of trace elements between co-crystallized BMS in hydrothermal ores is not well constrained. This is in contrast to the generally well understood partitioning behaviour of trace elements, including the platinum group elements and gold, between pyrrhotite, pentlandite, pyrite and BMS in magmatic sulphide ore deposits (e.g., Holwell and McDonald, 2010; Dare et al., 2011, and references therein).

Previous work that addresses trace element concentrations within individual sulphides has demonstrated the need to understand trace element partitioning patterns in hydrothermal BMS assemblages. This study aims to identify whether trace element partitioning between co-crystallized sphalerite, galena and chalcopyrite is predictable, and if so, to determine the primary controls on this partitioning. Such information can underpin tools for assessing whether a given BMS assemblage co-crystallized, and also potentially to enable constraints to be placed on conditions of BMS co-crystallization. In this contribution, we acknowledge the role that temperature, pressure, redox conditions at

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time of crystallization and metal source have on partitioning trends, but will emphasize the important role played by trace element oxidation state and, closely related to that, ionic radius.

## 2. Background

George et al. (2015) presented a reconnaissance study of trace elements in galena and showed that a range of elements are systematically hosted in solid solution within galena from SEDEX, epithermal, skarn, VMS, orogenic Au and porphyry BMS ores. A number of these elements show predictable behaviours when preferentially partitioning into galena together with other elements via coupled substitution (e.g., Bi and Sb with Ag, Tl and Cu), as well as systematic partitioning between two coexisting minerals (e.g., Tl between galena and sphalerite). It was, however, also noted that the presence or absence of other co-existing sulphides can influence the distributions of some trace elements within some deposit types (e.g., Sn distribution patterns in galena from recrystallized massive sulphide deposits containing chalcopyrite). It is thus difficult to make broad conclusions about the partitioning behaviour of trace elements when galena is largely considered in isolation. In order to gain a more accurate understanding of the partitioning behaviour of trace elements between two or more co-crystallizing BMS in a given ore system, the chemistry of any sulphide phase needs to be considered in the context of the complete BMS assemblage. In light of this, the present study sets out to answer the following question: do trace elements exhibit predictable partitioning behaviours among sphalerite, galena and chalcopyrite when the three minerals co-crystallize?

One of the outcomes of contemporary *in-situ* microanalytical investigation of sulphides is the recognition that many sulphides previously considered homogenous at the grain-scale, are in fact not always so (e.g., molybdenite; Ciobanu et al., 2013). Thus some published trace element datasets, especially those obtained before the 1980s, may simply represent averages of multiple, compositionally-distinct zones within a single grain. Recognition of elements present in solid solution, or occurring in micro-inclusions of distinct mineral phases, has been traditionally gained by carefully assessing all element concentrations and seeking combinations of elements that suggest inclusions [e.g., proton microprobe work of Cabri et al. (1985) or Huston et al. (1995)]. The LA-ICP-MS technique, however, may provide indirect evidence for the presence of micro-inclusions. If these are large enough and heterogeneously distributed, they will be recognized on time-resolved down-hole ablation profiles (e.g., George et al., 2015). The ability to distinguish a trace element in solid solution from one occurring as nano- to microscale inclusions of a distinct mineral phase is critical for interpretation of such data since it is likely that only those trace elements that are substituted into the crystal lattice of a sulphide would reveal systematic partitioning patterns. The LA-ICP-MS mapping technique allows for a visual comparison of multiple compositionally-distinct zones within a single grain or co-existing assemblage. Assuming such zoning occurs at a scale larger than the spatial resolution, even trace element heterogeneity may be recognized. LA-ICP-MS also offers advantages over SIMS in that the technique is more flexible with standards, significantly cheaper to run, and perhaps most importantly, offers simultaneous analysis of >25 elements.

Despite some of the limitations of modern microanalysis discussed, a review of the published literature provides a background to the data reported here. Table 1 summarizes the range of trace elements measured within sphalerite, galena and chalcopyrite and their typical concentrations as determined from analysis of natural specimens. The table also lists the experimentally-determined solubility limits of several of these elements.

## 3. Sample suite

The study covered 17 BMS-bearing samples from nine different skarn, epithermal and SEDEX deposits in Australia, Norway and Romania

(Table 2 and references therein). Selected samples contain coexisting sphalerite and/or galena and/or chalcopyrite, which textural evidence suggests co-crystallized at equilibrium. SEDEX deposits metamorphosed at greenschist facies (Fig. 1A) retain primary syn-sedimentary textures while epithermal (Fig. 1B) and skarn (Fig. 1C) systems commonly display 120° triple junctions between sulphide grains. Such grain boundaries are similar to those in SEDEX deposits metamorphosed at amphibolite facies and above (Fig. 1D, E) which display a coarser grain size and characteristic 120° triple junctions developed during equilibrium recrystallization. Though the sample suite is not representative of entire mineral associations in each different deposit, the samples were selected because they represent the same co-crystallized BMS assemblage formed at different physiochemical conditions in different ore types. They are thus representative for the purposes relevant to this study.

Skarn ores are represented by 5 samples from Baita Bihor and Oravita, two deposits located ~350 km apart along the Late Cretaceous Banatitic Magmatic and Metallogenetic Belt, Romania (BMMB; e.g., Ciobanu et al., 2002). The BMMB contains a range of magmatic-hydrothermal mineralization styles relating to the same magmatic event, and formed in subduction settings during Neotethys closure. The belt is well known for exotic trace mineral signatures including a most prominent Bi-mineral signature (e.g., Ciobanu et al., 2002). The Cu–Mo–Pb–Zn skarn deposit at Baita Bihor boasts the most complex geochemical signature [Bi–Ag–W–Se–Te–Ni–Co–Sn] among the deposits considered here. Consequently, this skarn exhibits a diverse sulphide mineralogy, including As-, Sb-, and Bi-sulphosalts and Bi- and Ag-tellurides (Cioflica et al., 1995, 1997; Cook and Ciobanu, 2003; Ilinca et al., 2012; Ciobanu et al., 2014). The Antoniu orepipe is Cu-dominant and proximal to the granitoid-derived source fluids. It contains Pb–Zn ores near the marble/skarn contact and lesser amounts within the Cu zone. The distinctly Pb–Zn Marta orepipe is a distal zone, ~1.2 km ENE from Antoniu.

Oravita is one of the many Cu–Au skarns that are satellite to porphyry Cu–Mo-intrusions within the Banat region (SW Romania and Serbia), known for its rich deposits (e.g., von Cotta, 1864). As with many Cu skarns, it also contains base metal ores and minor W-mineralization (Gheorghitescu, 1975; Cioflica and Vlad, 1981; Constantinescu et al., 1988). Oravita is one of the few localities where gehlenite skarns are known along the BMMB (Katona et al., 2003; Marinca et al., 2011). Although such skarns are barren, they provide an upper temperature limit (~750 °C) for initiation of the skarn system close to intrusion contacts.

Four samples come from Herja and Toroiaga, Baia Mare District, Romania. Both deposits are polymetallic epithermal vein systems of Neogene age with a diverse mineralogy, including well-known occurrences of Pb–Ag–Sb–As or -Bi sulphosalts. Cu–Au–Pb–Zn veins at Toroiaga are located 90 km to the east of the Pb–Zn–Ag veins at Herja, but related to the same regional-scale E–W-trending Dragos Voda fault (Neubauer et al., 2005 and references therein). Toroiaga is somewhat distinct from other deposits in the Baia Mare District in that its veins are thought to have formed at higher temperatures (as much as 400 °C; Cook, 1997), i.e., unlike the typical Pb–Zn–Ag veins common in Baia Mare.

Eight samples have been selected from five SEDEX deposits (Table 2). These are divided into two groups based on metamorphic grade. Only those deposits metamorphosed at conditions above greenschist facies show clear textural evidence for recrystallization of the BMS assemblage (e.g., coarse annealed textures, commonly with 120° triple junctions between grains; Fig. 1D, E). Recrystallization allows for pervasive re-partitioning of trace elements from the primary low-temperature SEDEX distributions to the distributions preferred at high metamorphic temperatures and pressures, followed by slow cooling. Recrystallized SEDEX deposits (5 samples) can thus be distinguished from those of lower metamorphic grades (3 samples).

Those SEDEX deposits of lower metamorphic grade include Kapp Mineral and Mt. Isa. Kapp Mineral is a minor occurrence from the Hecla Hoek Complex, Svalbard Archipelago, Norway. Mineralization is of an undetermined, possibly late Precambrian age but has clearly

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