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## Trace Element Distributions in Sulphides: Progress, Problems and Perspectives

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### 1 Introduction

Multi-trace element analysis of trace elements in sulphide minerals has become commonplace in ore genesis studies (e.g., Reich et al., 2013). Among other contemporary methods, laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) instrumentation provides rapid, accurate data with sub-ppm sensitivity coupled with good spatial resolution. The volume of published LA-ICP-MS trace element data for common sulphides (pyrite, arsenopyrite, sphalerite, chalcopyrite, galena, bornite, chalcocite and molybdenite) in all types of ore deposits is accordingly growing at a rapid rate.

Trace element data for sulphide minerals is applied in geometallurgy (chiefly element deportment studies in processing and waste management), and in studies of ore genesis. Sulphide geochemistry also shows potential in the development of innovative exploration methods, particularly in the near-mine environment.

From a scientific perspective, the past decade has seen significant advances in quantifying the ranges of trace element concentrations present in individual mineral species. There has also been an expansion of empirical evidence for systematic patterns of trace element partitioning among co-existing minerals. This understanding has been complemented by better appreciation of the chemical state of trace elements hosted in sulphides (e.g., Cook et al., 2012; Belissont et al., 2014), the substitution mechanisms facilitating their incorporation (e.g., Deditius et al., in press), the role of nanoparticles (e.g., Ciobanu et al., 2012), and the often critical interplay between trace element substitution, compositional zoning and crystal structure at the lattice-scale (e.g., Ciobanu et al., 2011).

This contribution briefly describes recent results and outlines a number of outstanding issues and future research opportunities in the field.

### 2 Recent Developments

#### 2.1 Trace element data for galena and chalcopyrite

LA-ICP-MS analysis of galena in 36 samples from 24 mineral deposits of different types (George et al., in press) has shown that Ag, Bi and Sb are the most common trace elements in the Pb-sulphide; each exceeding 0.5 wt.% in some samples. Copper, Tl, Cd, Se and Sn are also present at measurable concentrations; rarely also Te. Copper and Tl appear to correlate well with (Bi+Sb), supporting incorporation via coupled substitution:  $2\text{Pb}^{2+} \leftrightarrow (\text{Ag,Cu,Tl})^+ + (\text{Sb,Bi})^{3+}$ . Galena may be a hitherto unrecognised Sn-carrier in some deposits. Gold, Hg, Mn, Co, Ni, Zn, Ga, As or Mo are not present at concentrations >1 ppm. Low-temperature epithermal galena displays spectacular oscillatory and sectorial zoning with respect to Ag, Sb, Bi and Se.

Preliminary trace element datasets for chalcopyrite reveals the mineral to be a good host for Ag and, in some cases, Sn, and a poorer host for In than co-existing sphalerite. Distribution patterns vary with the relative abundance of coexisting sphalerite and galena. We find no evidence for incorporation of Bi in chalcopyrite – an observation relevant for the fact that Bi enrichment in copper concentrates may incur penalties from the buyer or smelter. No evidence has thus far been found for compositional trace element zoning in chalcopyrite.

#### 2.2 Partitioning patterns among base metal sulphides

We have generated LA-ICP-MS element maps of galena (Gn)-sphalerite (Sp)-chalcopyrite (Cp) assemblages in (a) epithermal vein ores and (b) VMS/SEDEX deposits metamorphosed at middle amphibolite grade or higher. In both cases, textures are judged to indicate crystallization at equilibrium. Preferred host minerals are, for In, Mn, Ga and Ge: Sp>Cp>Gn; for Hg and Cd: Sp>Gn>Cp; and for Bi, Sb, Se and Te: Gn>>(Sp,Cp). Gold, Co, Ni and As are always concentrated in co-existing pyrite and/or arsenopyrite

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(where present) relative to the base metal sulphides. The partitioning behaviour of Ag and Sn in multi-component systems is less consistent, and the subject of ongoing study. Thallium is commonly concentrated in galena, but like Ga, may also be relatively enriched in pyrite.

### 3 Outstanding Problems

#### 3.1 What are we analysing?

LA-ICP-MS analysis is normally carried out on areas of a mineral grain in which the surface is deemed free of visible inclusions. It is, however, a technique in which the analysed volume of sample material can be several thousand  $\mu\text{m}^3$  (e.g., a spot diameter of 30  $\mu\text{m}$ , crater depth of 15–20  $\mu\text{m}$  – potentially more for softer minerals such as galena), leaving room for analysis of a micro-volume that is potentially heterogeneous.

A scanning electron microscope (SEM), operated in back-scatter electron mode, is generally used for pre-selection of the areas to be analysed, inferring that the minimum observable size of inclusions is at best  $\sim 0.2 \mu\text{m}$ , dependent on the resolution of SEM instrument used and the skill of the operator. The inference is that if smaller inclusions of nanoparticle size ( $< 200 \text{ nm}$ ) are present, they will likely not be seen on the BSE images.

#### 3.2 Solid solution or finely-dispersed nanoparticles?

Although less critical in element deportment studies, a long-standing problem, with implications for ore genesis, remains how to distinguish between elements in solid solution within the host mineral, and those occurring as inclusions of discrete minerals at the sub-micron to nanoscale. Arguments based on the smoothness of the LA-ICP-MS down-hole signal or size of the substituting ion relative to that which is being replaced, although useful, cannot always provide unequivocal answers.

Instruments such as the focussed ion beam (FIB)-SEM have opened up new ways of preparing small volumes of sample *in-situ* for analysis by TEM (Ciobanu et al., 2011). This provides an excellent way to confirm if nanoparticles are potentially present in the immediate vicinity of LA-ICP-MS craters.

#### 3.3 Raising standards

Although matrix-matched standards have become widely available in recent years, there are still a number of unresolved questions about their broad applicability. Questions centre on whether there are matrix effects associated with the use of a single standard for different sulphide minerals, and whether standards that contain only low ppm levels of a given element can be reliably used for minerals in which that element is major and serves as an

internal standard.

## 4 Research Opportunities

#### 4.1 From empirical observation to predictive tool

Empirical observations of trace element concentrations in coexisting sulphide assemblages suggest there must be systematic, measurable patterns of element distribution (e.g., behaviour of Ag and Bi in bornite-chalcocite pairs). This implies they may carry potential as geothermometers or other tools of petrogenetic value. Additional data are necessary to verify the trends, and need to be complemented by synthetic experiments and/or numerical modelling.

#### 4.2 New methods for data treatment

The efficiency and speed at which LA-ICP-MS data can be acquired offers unparalleled opportunities to collect sizeable datasets that can be systematically viewed using statistical routines of varied sophistication. The criticality of selecting statistical techniques appropriate to each dataset was highlighted in a reconnaissance study that applied different multivariate statistical techniques to analyse distribution patterns in a trace element LA-ICP-MS dataset for pyrite (Winderbaum et al., 2013).

Datasets currently acquired are typically far larger than this, allowing for more precise modelling of complex numerical patterns, particularly those containing extreme values. The development of mathematical-statistical routines necessary for proper interpretation of that data is an increasingly active research area. Particularly when seeking to identify patterns within a given ore system that could allow for the development of exploration vectors for near-mine exploration, a sound statistical foundation is essential. Without being able to mathematically model patterns within the data, and lacking access to, and understanding of statistical models that account for the inherent variability and underlying relationships within such a dataset, the full value of that dataset may not be fully appreciated. Further data treatment issues include statistical modelling of concentration values  $< \text{mdl}$ .

#### 4.3 Expansion to sulphide-oxide-silicate assemblages

Although it is correctly assumed that most metallic elements will be preferentially incorporated into sulphides, we emphasize that the role played by oxides, (and to some extent silicates) in the deportment of certain elements may be understated. An illustrative example is the enrichment of Mo, W and U in sector-zoned hematite from the Olympic Dam IOCG deposit, South Australia (Ciobanu et al., 2013). In the same metallogenic province, skarn garnet in the Groundhog Cu-Au prospect has been found to host up to

thousands of ppm of W, Sn, U, As, and in some cases, measurable concentrations of rare elements such as In.

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