TRACE ELEMENT DISTRIBUTIONS AND PARTITIONING TRENDS IN HYDROTHERMAL BASE METAL SULPHIDE ORES COMPRISING SPHALERITE, GALENA, CHALCOPYRITE AND TETRAHEDRITE-TENNANTITE

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ABSTRACT

This study addresses trace element concentrations and distributions in hydrothermal base metal sulphide (BMS) ores using samples from a wide variety of ore deposits and conditions of ore formation. The ranges of trace elements that can be incorporated into natural sphalerite, galena, chalcopyrite and tetrahedrite-tennantite are determined, as are the preferred equilibrium trace element partitioning trends among these sulphides.

The previously documented coupled substitution $Ag^{+}+(Bi, Sb)^{3+} \leftrightarrow 2Pb^{2+}$ in galena is confirmed, yet should also be modified to include Cu^{+} and Tl^{+}. However, when Bi and/or Sb are present at concentrations above ~2000 ppm, incorporation likely includes the creation of site vacancies. Thallium is always principally hosted in galena when BMS assemblages including sphalerite and chalcopyrite are mapped with LA-ICP-MS. Trace element mapping also reveals oscillatory and sector compositional zoning of various elements in galena for the first time. It is inferred that the partitioning of certain minerals between galena and sphalerite pairs is both predictable and systematic.

This systematic partitioning is explored and it is shown that the primary factors controlling the preferred BMS hosts of almost all trace elements in sphalerite-galena-chalcopyrite assemblages are element oxidation state, ionic radii of the substituting elements, element availability and the maximum trace element budget that a given sulphide structure can accommodate. In contrast, it is revealed that temperature, pressure, redox conditions at time of crystallization and metal source, do not significantly affect the preferred BMS host of almost all trace elements. The only exceptions to this recognized in the study are the critical metals Ga, In and Sn in assemblages recrystallized at high metamorphic grades. Observed partitioning patterns can be used to assess whether a particular BMS assemblage co-crystallized.

Compared to sphalerite and galena, trace element concentrations in chalcopyrite are typically quite low (tens to hundreds of ppm). Nevertheless, it is shown that chalcopyrite can host a wide range of trace elements, and the concentrations of such elements generally increase in chalcopyrite in the absence of other co-crystallizing sulphides. Importantly, chalcopyrite is generally a poor host for most elements considered harmful or unwanted in the smelting of Cu (except for Se and Hg on occasions), which suggests it is rarely a significant contributor to the presence of such elements in copper concentrates. The concentrations of Zn and Cd in chalcopyrite show systematic variation that depends, at least in part, on the temperature of BMS crystallization. The Cd:Zn ratios in coexisting chalcopyrite and sphalerite may be used to assess if the physiochemical conditions remained constant during BMS crystallization.

Since minerals of the tetrahedrite isotypic series are also common components in base metal ores, investigation into the trace element chemistry of tetrahedrite-tennantite is relevant to understanding the controls on trace element partitioning in such ores. It is shown that tetrahedrite-tennantite will always be the primary host of Ag, Fe, Cu, Zn, As and Sb, and will be the secondary host of Cd, Hg and Bi in co-crystallizing BMS assemblages. Conversely, tetrahedrite-tennantite is a poor host for the critical metals Ga, In and Sn, all of which will prefer to partition to co-crystallizing BMS.

DECLARATION

I certify that this work, to the best of my knowledge, contains no material previously published or written by another person, except where due reference has been made in the text, and that, unless otherwise indicated (see preface), no material has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of The University of Adelaide and, where applicable, any partner institution responsible for the joint-award of this degree.

I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

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Signed ____________________________ Date 26/05/17

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"To know the mighty works of God, to comprehend His wisdom and majesty and power; to appreciate, in degree, the wonderful workings of His laws, surely all this must be a pleasing and acceptable mode of worship to the Most High, to whom ignorance cannot be more grateful than knowledge."

-Nicolaus Copernicus

PREFACE

This thesis comprises of a portfolio of manuscripts which have been published, or accepted for publication, in international peer-reviewed journals. The journals in which these papers have been published and/or accepted are *'American Mineralogist'* (Chapter 3), *'Ore Geology Reviews'* (Chapter 4), *'Mineralogical Magazine'* (Chapter 5) and *'Minerals'* (Chapter 6). All of the manuscripts are closely related, and summarise the sulphide trace element analytical data, observations and interpretations that were made as part of this project. Recommendations have been made at the end of this thesis as a direct result of the key findings of this research, and it is hoped that many of these are explored at a later date.

The four papers which form the basis of this thesis are:

1. George, L., Cook, N. J., Ciobanu, C. L., Wade, B. P., 2015. Trace and minor elements in galena: A reconnaissance LA-ICP-MS study. American Mineralogist 100, 548-569. (*This paper builds on research undertaken during the candidate's honours year.)*

2. George, L. L., Cook, N. J., Ciobanu, C. L., 2016. Partitioning of trace elements in co-crystallized sphalerite–galena–chalcopyrite hydrothermal ores. Ore Geology Reviews 77, 97-116.

3. George, L. L., Cook, N. J., Crowe, B. B. P., Ciobanu, C. L., 2017. Trace elements in hydrothermal chalcopyrite. Mineralogical Magazine (accepted for publication at time of thesis submission).

4. George, L. L., Cook, N. J., Ciobanu, C. L., 2017. Minor and trace elements in natural tetrahedrite-tennantite: effects on element partitioning among base metal sulphides. Minerals 7, 17. doi: 10.3390/min7020017.

Chapter 8 contains all additional material* for the main papers outlined above, as well as additional conference abstracts, and other co-authored publications that have been produced. The additional material is as follows:

A. Additional material for Chapter 3 (Paper 1).

B. Additional material for Chapter 5 (Paper 3).

C. Additional material for Chapter 6 (Paper 4).

D. Cook, N., Ciobanu, C. L., George L., Zhu Z. Y., Wade B., Ehrig K., 2016. Trace element analysis of minerals in magmatic-hydrothermal ores by laser ablation inductively-coupled plasma mass spectrometry: Approaches and opportunities. Minerals 6, 111. doi: 10.3390/min6040111.

E. George, L. L., Cook, N. J., Ciobanu, C. L., 2016. Trace element partitioning between sphalerite, galena and chalcopyrite (Abstract). 35th International Geological Congress, Cape Town, South Africa, August 27th – 4th September.

F. George, L., Cook, N., Ciobanu, C., 2015. Controls on trace element partitioning between sphalerite and galena (Abstract and Poster). Society of Economic Geologists Conference 2015, ‘World-Class Ore Deposits: Discovery to Recovery’, Hobart, TAS, Australia, September 27th – 30th.

* Appendix A for Chapter 4 (Paper 2) may be found in Chapter 4

G. George, L., Cook, N. J., Ciobanu, C. L., 2015. Trace element partitioning between co-existing sphalerite, galena and chalcopyrite (Extended abstract). In: André-Meyer, A. -S., et al., Eds., Mineral Resources in a Sustainable World. Proceedings of the 13th SGA Biennial Meeting, Nancy France, ISBN: 978-2-85555-065-7, 24-27.

H. Cook, N. J., Ciobanu, C. L., George, L. L., Crowe, B., Wade, B. P., 2014. Trace Element Distributions in Sulphides: Progress, Problems and Perspectives (Extended abstract), 14th Quadrennial Symposium of the International Association on the Genesis of Ore Deposits, 'Mineral Resources: Discovery and Utilization, "Let's brainstorm"', Kunming, China 19th – 22nd. August 2014, Acta Geologica Sinica (English Edition) 88, 1444-1446.

The final chapter of this thesis consists of a complete reference list of all publications cited within any of the manuscripts, chapters and additional material of this thesis.