In situ multiple sulfur isotope analysis by SIMS of pyrite, chalcopyrite, pyrrhotite, and pentlandite to refine magmatic ore genetic models

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ABSTRACT

With growing interest in the application of in situ multiple sulfur isotope analysis to a variety of mineral systems, we report here the development of a suite of sulfur isotope standards for distribution relevant to magmatic, magmatic-hydrothermal, and hydrothermal ore systems. These materials include Sierra pyrite (FeS_2), Nifty-b chalcopyrite ($CuFeS_2$), Alexo pyrrhotite ($Fe_{(1-x)}S$), and VMSO pentlandite ($(Fe,Ni)_9S_8$) that have been chemically characterized by electron microprobe analysis, isotopically characterized for $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$ by fluorination gas-source mass spectrometry, and tested for homogeneity at the micro-scale by secondary ion mass spectrometry. Beam-sample interaction as a function of crystallographic orientation is determined to have no effect on $\delta^{34}S$ and $\Delta^{33}S$ isotopic measurements of pentlandite. These new findings provided the basis for a case study on the genesis of the Long-Victor nickel-sulfide deposit located in the world class Kambalda nickel camp in the southern Kalgoorlie Terrane of Western Australia. Results demonstrate that precise multiple sulfur isotope analyses from magmatic pentlandite, pyrrhotite and chalcopyrite can better constrain genetic models related to ore-forming processes. Data indicate that pentlandite, pyrrhotite and chalcopyrite are in isotopic equilibrium and display similar $\Delta^{33}S$ values +0.2‰. This isotopic equilibrium unequivocally fingerprints the isotopic signature of the magmatic assemblage. The three sulfide phases show slightly variable $\delta^{34}S$ values ($\delta^{34}S_{chalcopyrite} = 2.9 \pm 0.3‰$, $\delta^{34}S_{pentlandite} = 3.1 \pm 0.2‰$, and $\delta^{34}S_{pyrrhotite} = 3.9 \pm 0.5‰$), which are indicative of natural fractionation. Careful in situ multiple sulfur isotope analysis of multiple sulfide phases is able to capture the subtle isotopic variability of the magmatic sulfide assemblage, which may help resolve the nature of the ore-forming process. Hence, this SIMS-based approach discriminates the magmatic sulfur isotope signature from that recorded in metamorphic- and alteration-related sulfides, which may not be resolved during bulk rock fluorination analysis. The results indicate that, unlike the giant dunite-hosted komatiite systems that thermo-mechanically assimilated volcanogenic massive sulfides proximal to vents and display negative $\Delta^{33}S$ values, the Kambalda ores formed in relatively distal environments assimilating abyssal sulfidic shales.

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1. Introduction

Sulfur is a trace element in silicate melts, typically concentrated below 0.2 wt%. However, it is an essential element in a wide range of environments including the lithosphere, biosphere, hydrosphere, and atmosphere. In recent years, our understanding of the sulfur cycle and its role in the evolution of these terrestrial reservoirs has been revolutionised by the study of the sulfur isotope composition of pyrite,

the most common sulfide mineral (Farquhar et al., 2000; Kump, 2012 and references therein; Strauss, 1997; Thomassot et al., 2015). We have gained a fundamental understanding into the development of early Earth's processes, in particular those linked to the emergence of life and the development of an oxygenated atmosphere (Farquhar et al., 2000), by the discovery of mass independent fractionation (MIF) of sulfur isotopes.

Sulfur resides in the Earth's mantle, crust and hydrosphere but is locally concentrated in mineralised systems typically associated with ore deposits, where it acts as the primary complexing ligand in the formation of sulfide minerals. Mantle- and crustally-derived magmas have

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brought large quantities of economic metals from the Earth's interior to the near surface, and hydrothermal fluids have remobilised and re-precipitated these metals within the crust as different sulfides. The sulfur itself may be sourced from a variety of compositional reservoirs, each with distinct isotopic compositions. Mixing and interactions with the mantle, crustal magmas, hydrothermal fluids, country rocks, or meteoric waters imparts specific isotopic signatures, resulting in minerals with a range of isotopic compositions. As such, intra-grain and inter-grain chemical and isotopic variations in sulfur-rich mineralised systems record the interaction of these different reservoirs and offer unique insights into the complex fluid-rock interactions within mineral systems (McCuaig et al. 2010). For example, in magmatic ore deposits, sulfur isotope data have fingerprinted the source of the sulfur linked to ore genesis (Bekker et al., 2009; Chang et al., 2008; Fiorentini et al., 2012a; Hiebert et al., 2013; Lesher and Groves, 1986; Penniston-Dorland et al., 2008; Sharman et al., 2013) and constrained the geodynamic framework where these deposits formed (e.g., Chen et al., 2015; Fiorentini et al., 2012b; Giacometti et al., 2014). Similarly, sulfur isotope studies have proven to be vital in characterising magmatic-hydrothermal (Helt et al., 2014; Xue et al., 2013) and hydrothermal systems (e.g., Jamieson et al., 2013; Leach et al., 2005; Sharman et al., 2015). Constraining the sulfur isotopic signature in magmatic-hydrothermal mineral systems is useful in delineating the source of sulfur, and is an important parameter to understand how, when and where sulfur saturation occurs (e.g., Evans et al., 2014). In addition, such data provides a better understanding of the geodynamic environment in which the mineralising process occurs which impacts on the targeting rationale applied during exploration (e.g., Fiorentini et al., 2012a). Consequently, ore deposits are a perfect laboratory for understanding the source and mobility of sulfur in a wide variety of settings.

Mineral systems and ore deposits have characteristically complex microscale intra-granular and inter-granular textures due to variations in their chemistry during formation and subsequent re-equilibration during cooling (e.g., pentlandite exsolution in pyrrhotite; Durazzo and Taylor, 1982). In situ sulfur isotope analysis at the microscale has the potential to revolutionise our understanding of ore forming processes. The development of in situ analytical techniques using laser ablation-(multi-collection)-inductively coupled plasma mass spectrometry (LA-MC-ICPMS; see Bühn et al., 2012; Craddock et al., 2008) and large geometry secondary ion mass spectrometry (SIMS; see Farquhar et al., 2013; Ireland et al., 2014; Ushikubo et al., 2014; Whitehouse, 2013) now allows high-precision isotopic analysis of multiple sulfur isotopes with spot sizes nearing ten microns. The ultra-high sensitivity of SIMS in particular affords the ability to measure the least common stable isotopes of sulfur, ^{33}S (0.75%) and ^{36}S (0.02%), together with the more abundant ^{32}S (95.02%) and ^{34}S (4.21%) isotopes, simultaneously from the same volume of material. This gives the potential to identify the anomalous sulfur isotopic signatures indicative of mass independent fractionation (MIF; $\Delta^{33}S$ and $\Delta^{36}S$ together with $\delta^{34}S$.

Instrumental mass fractionation in SIMS is intrinsically linked to the composition and crystallographic orientation of the material being analysed and the specific conditions under which the analysis is performed. Therefore, accurate isotopic measurements require careful standardization against a suitable matrix-matched reference material (Eiler et al., 1997; Stern, 2008). Although a number of reference materials have been developed for acquiring in situ 2-sulfur isotopes (e.g., Kozdon et al., 2010), the majority of published in situ 3- or 4-sulfur isotope analyses have been acquired from the most common sulfide mineral, pyrite. As such, many SIMS laboratories worldwide have developed "in-house" pyrite (and to a lesser degree other) standards for multiple sulfur isotope analysis (Balmat, Isua 248474, Ruttan; see Whitehouse, 2013; Ushikubo et al., 2014; Hauri et al., 2016). With growing interest in the application of in situ sulfur isotope analysis to a wide variety range of mineral systems, there is an increased need for reference material for a variety of common sulfide minerals, which presently remain scarce. In addition to composition, sulfide crystallography has

previously been demonstrated to potentially create an orientation effect-induced instrumental mass bias on sulfur isotope analysis for certain sulfides including galena (PbS) and sphalerite ((Zn,Fe)S) but not others including pyrite (FeS$_2$), pyrrhotite (Fe$_{(1-x)}$S), and chalcopyrite (CuFeS$_2$) (Kozdon et al., 2010; Kita et al., 2011). Of these sulfides, most have a diamond-cubic crystal structure, with the exception of galena which has a cubic hexoctahedral structure. Here, we build on this observation to demonstrate that orientation effect does not induce instrumental mass fractionation on $\delta^{34}S$ and $\Delta^{33}S$ in another cubic hexoctahedral sulfide - pentlandite ((Fe,Ni)$_9$S$_8$).

Deviations from mass dependent fractionation are typically (but not uniquely) triggered by the presence of an oxygen-poor atmosphere that existed before the Great Oxidation Event at ca. 2.4 Ga in which ultraviolet radiation was the driver for mass independent photochemical separation of sulfur isotopes (e.g., Farquhar et al., 2000; Farquhar and Wing, 2003). For this reason, the measure of ^{33}S has become essential to evaluate the full suite of isotopic features of Archean rocks (e.g., Bühn et al., 2012; Farquhar et al., 2013), and those from younger terranes that might be sourcing Archean rocks (e.g., Cabral et al., 2013). The least abundant stable isotope of sulfur, ^{36}S, behaves similarly to ^{33}S, and has also become increasingly important for fingerprinting Archean source rocks and understanding early Earth processes. The $\Delta^{36}S/\Delta^{33}S$ ratio can elucidate between mass dependent processes and contributions from Archean MIF sources when magnitudes of mass dependent fractionation deviations are small (Farquhar et al., 2007; Johnston, 2011).

We present multiple sulfur isotope data from pentlandite, pyrrhotite, and chalcopyrite from an Archean komatiitic massive nickel-sulfide deposit. To do so, we have developed four reference materials (pyrite, chalcopyrite, pyrrhotite, and pentlandite) that we have fully chemically and isotopically characterized for multiple sulfur isotope analysis. We present multiple sulfur isotope results from multiple sulfides within the deposit to constrain the source of the sulfur that triggered sulfide saturation and investigate the geodynamic setting in which this magmatic system was emplaced.

2. Methods

To determine the chemical and isotope composition of potential sulfide reference materials we combined three analytical techniques. Firstly, we performed wavelength dispersive spectrometry (WDS) by electron probe micro-analysis (EPMA) on a multitude of grains (or grain fragments) of each candidate reference material to ensure that the reference material is chemically homogeneous across a number of grains (or grain fragments). Chemical compositions (spot analyses) were linked to chemical WDS maps and scanning electron microscope backscatter electron (SEM-BSE) images to highlight potential chemical zonation, mineralogical inclusions, and fractures. Details of SEM-BSE and EPMA-WDS are presented in the Supplementary Material.

Secondly, at least five grains (or grain fragments) of each candidate reference material were analysed for in situ multiple sulfur isotopes by SIMS to determine whether an adequate level of reproducibility exists at the intra- and inter-grain scale (isotopic homogeneity). Multiple materials were tested prior to selecting the material that displayed adequate isotopic homogeneity (reproducibility on $^{34}S/^{32}S$ better than 0.5‰). For instance, five materials from different environments were tested to find a suitable chalcopyrite standard (see Section 5.1 for discussion on selecting sulfide reference material). To further determine on what scale sufficient homogeneity existed once the reference material was selected, >40 grains for each material were analysed. If the reference material was deemed suitable, multiple grains or grain fragments (in the case of material derived from large crystals) were analysed by bulk multiple sulfur analyses. Bulk analyses were completed by fluorination gas-source mass spectrometry. In each case, sulfur was extracted from 5 to 11 separate aliquots (of extracted sulfur from separate grains or grain fragments) and analysed for its multiple sulfur isotopic composition. We further evaluated the homogeneity of the