Sulfur isotope signatures in the lower crust: A SIMS study on S-rich scapolite of granulites

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Abstract

Scapolite is an important reservoir for volatiles in the deep crust and provides unique insights into the S isotope signatures at the mantle/crust interface. Here, we document the first scapolite reference material (herein referred to as CB1) for in situ S isotope analysis. The chemical and isotope composition of this euhedral, S-rich scapolite megacryst was characterized via LA-ICP-MS, EPMA, SIMS, and bulk fluorination gas source isotope ratio mass spectrometry. The CB1 scapolite is isotopically homogeneous and our results show that crystal orientation does not affect in situ S isotope SIMS analysis. This makes CB1 an ideal primary calibration standard for in situ analysis of S isotope ratios ($^{36}\text{S}/^{32}\text{S}$, $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$) in scapolite. With this reference material in hand, we then applied in situ SIMS

analysis of S isotopes for the first time on scapolite in granulite samples from the lower crust/upper mantle. The analysed sample suite comprises rocks from classic granulite xenolith locations in southeastern Australia, as well as a sample from the high-grade suture zone of the Dahomeyides in south-eastern Ghana. The results show that scapolites in the lower crust have $\delta^{34}\text{S}$ values between ~ -0.5 and $+4$ (‰ VCDT). These values fall within the range of S isotope signatures present in mantle rocks and provide no evidence for the recycling of seawater-derived S into the lower crust. We propose that scapolite formed during granulite facies metamorphism of igneous cumulates, where S was sourced from precursor igneous sulfides. Sulfur isotope heterogeneities between individual scapolite grains in some of the studied samples may reflect non-uniform S-isotope compositions of igneous S-phases, which precipitated from mantle-derived melt.

1. Introduction

The global S cycle is of multidisciplinary interest, as it addresses questions concerning the evolution of the atmosphere including its oxygen balance, the evolution of early life on Earth (e.g., [Canfield, 2004 and references therein](#)) as well as the formation of ore-deposits throughout the Earth's history (e.g., [Benning and Seward, 1996](#)). While surface or shallow subsurface processes involving S distribution and fluxes can be studied and monitored in great detail (e.g., [Canfield, 2004](#)), S behaviour in the crust and mantle is more challenging to comprehend. Previous studies have shown that the recycling of S via subduction might be a key process in the global S cycle (e.g., [Alt et al., 1993; 2012; Wallace, 2005](#)) and important for the redox budget of the mantle (e.g., [Alt et al., 2012; Evans and Powell, 2015](#)). Our current understanding is that significant amounts of S, as sequestered in seawater, sediments, and altered (oceanic) crust, is recycled via subduction and arc magmatism/volcanism ([Fig. 1](#)).

Variations in the stable isotope composition of S (i.e., $^{36}\text{S}/^{32}\text{S}$, $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$) compared to Vienna Cañon Diablo Troilite (VCDT) have been used as an essential tool for

tracking S fluxes and provenance during geodynamic processes (e.g., Sasaki and Ishihara, 1979; Alt et al., 1993; Cabral et al. 2013; Labidi et al., 2014). For instance, several studies have reported elevated values of $\delta^{34}\text{S}$ in subduction-related volcanic rocks (e.g., Sasaki and Ishihara, 1979; Ishihara and Sasaki, 1989; Alt et al., 1993) (Fig. 2). These phenomena might be attributed to fluids released from the subducting slab, derived from seawater and sulfates with strongly positive $\delta^{34}\text{S}$ values (+20 ‰, Fig. 2), which are recycled through the upper (sub-arc) mantle and overlying crust, eventually reaching the atmosphere via volcanic degassing (Fig. 1). However, using S isotopes to constrain subduction-related and global S mass transfer relies on how well we can constrain the different S reservoirs in terms of their S content and S isotope characteristics. While we have a general idea about the S isotope composition of subducted material (input) and arc magmas (output) (e.g., Alt, 1995; Marini et al., 2011 and references therein), one of the missing links for understanding the S cycle concerns the behaviour and isotope composition of S in the lower crust, at the mantle-lithosphere interface.

Rocks from the lower crust/upper mantle may be the key to better constrain the S isotope characteristics of slab-derived fluids. This is because the S isotope signatures of deep crustal rocks are less likely to be affected by interaction with supracrustal material and degassing reactions compared to volcanic samples, or rocks in the middle/upper crust (e.g., Sasaki and Ishihara, 1979; Ishihara and Sasaki, 1989).

Granulites affiliated with subduction zones are promising candidates for gaining insight into the S isotope signature of the lower crust, and for tracing potential S fluxes from the mantle and subducted slab (Fig. 1). Granulites are generally sulfide-deficient (Porter and Austrheim, 2016), however, metamorphic S-rich scapolite is widespread in lower crustal rocks (e.g., Knorring and Kennedy, 1958; Lovering and White, 1964; Goldsmith, 1976; Moecher et al., 1994; Yoshino and Satish-Kumar, 2001; Aulbach et al., 2010; Mansur et al., 2014; Porter and Austrheim, 2016) and is possibly a major rock-forming mineral in the lower

crust (e.g., [Lovering and White, 1964](#); [Goldsmith, 1976](#)). Scapolite in granulite/upper mantle xenoliths rapidly delivered to the surface by volcanic pipes with little to no retrogression might therefore provide a novel window into S sources and S isotope signatures in the lower crust ([Fig. 1](#)).

In this study, we measure S isotopes in scapolite formed at lower crustal conditions at high spatial resolution by secondary ionisation mass spectrometry (SIMS). Grains were analysed from petrographic thin sections, preserving textural context and allowing resolution of S isotope signatures on a micrometer-scale. We propose that in the case of scapolite, post-formation alteration and crustal contamination can be readily resolved by means of EPMA, LA-ICP-MS and SIMS analysis by targeting fresh cores of grains. The analysis of unaltered scapolite is particularly important for S isotope quantification, as sulfides might form as an alteration product ([Porter and Austrheim, 2016](#)), potentially leading to a significant S isotope fractionation that cannot be accounted for in bulk grain analysis. Our scapolite results fall within the same $\delta^{34}\text{S}$ range as previously found in mantle xenoliths studies, suggesting that seawater-derived S is unlikely to be a major component in the studied lower crustal samples. Furthermore, some of the studied samples show S isotope variations between individual scapolite grains, which we attribute to isotope heterogeneity of primary magmatic sulfides that acted as the major S source for scapolite formation during granulite facies metamorphism.

2. Background

Previous studies have improved the general understanding of S behaviour prior to and during subduction and associated magmatism. For instance, [Alt \(1995\)](#) showed that the $\delta^{34}\text{S}$ values of bulk altered oceanic crust ($\sim 0.9\text{‰}$) are only minimally different from their original basaltic source ($\sim 0.5 \pm 0.6\text{‰}$; e.g., [Sakai et al., 1984](#)). Other studies showed when and how S

is expected to be released due to mineral reactions during subduction, and how it might be recycled within the slab itself (Fig. 1) (Evans et al., 2014).

Alt et al. (1993) studied the S isotope signatures from the Mariana island arc and back arc basin and found that $\delta^{34}\text{S}$ is enriched (mean $\sim +3.8\text{‰}$ $\delta^{34}\text{S}$) in arc volcanic rocks, which they interpret to reflect a seawater S component in the sub-arc mantle source. The authors estimated that approximately one third of the S in arc magmas might be contributed by a metasomatic slab-derived fluid that mixed with mantle MORB-like S in the magma source region. Back-arc basalts on the other hand showed $\delta^{34}\text{S}$ values of $1.1 \pm 0.5\text{‰}$, which are similar to MORB values. These significantly lower values in back-arc basalts are attributed to the dilution of the slab S isotope signature in the predominantly unmetasomatized mantle source further from the arc. de Hoog et al. (2001) studied S isotope compositions in basaltic and basaltic andesitic lavas from the Indonesian arc. The study concluded that S is derived from a mantle source that is significantly enriched in $\delta^{34}\text{S}$ compared to typical MORB and OIB sources. The authors estimated that the magma sources had average $\delta^{34}\text{S}$ values between $+5$ and $+7\text{‰}$. These elevated $\delta^{34}\text{S}$ values are inferred to be a result of significant S transport by slab-derived fluids into the mantle wedge. Intriguingly, de Hoog et al. (2001) also showed that the range of $\delta^{34}\text{S}$ values in lavas is rather limited, despite the potentially large variations in S isotope composition of the subducted material.

Wilson et al. (1996) studied mantle xenoliths and found evidence of metasomatized mantle that led to elevated $\delta^{34}\text{S}$ isotopes values of up to $+7\text{‰}$, attributed to the subduction of crustal S. Ionov et al. (1992) examined a range of upper mantle xenoliths and their results show that most of their analysed peridotite xenoliths fall between -1 and $+4\text{‰}$ $\delta^{34}\text{S}$, with an overall average of $+2.1\text{‰}$ $\delta^{34}\text{S}$. These studies on mantle xenoliths imply non-uniform S isotope signatures in the mantle. Several other studies have also challenged the uniformity of the mantle S isotope composition. Chaussidon and Lorand (1990) have found evidence that

the upper mantle S isotope signatures might range from -3 to +3 ‰ $\delta^{34}\text{S}$, which can possibly explain S isotope variations in MORBs, alkali basalts and continental tholeiites. More recent work (Labidi et al., 2013, 2015; Cabral et al. 2013) also proposes variable and significantly depleted $\delta^{34}\text{S}$ values for MORBs, with a proposed depleted mantle end-member of ~ -1.3 ‰ (Labidi et al., 2013). OIBs on the other hand were found to range between strongly negative and positive $\delta^{34}\text{S}$ values (Cabral et al., 2013; Labidi et al., 2015) (Fig. 2). These findings of significant S isotope variations in the mantle reservoir further complicate the interpretation of S isotope compositions of arc magmas and middle crustal rocks.

The occurrence of scapolite at elevated P-T conditions has relevance for the sequestration of volatiles in lower crustal environments (e.g., Lovering and White, 1964; Goldsmith, 1976; Moecher et al., 1992). Scapolite stable at these conditions is typically enriched in C and/or S, approaching the meionite $\text{Ca}_4(\text{Al}_6\text{Si}_6\text{O}_{24})\text{CO}_3$ or silvialite compositions $\text{Ca}_4(\text{Al}_6\text{Si}_6\text{O}_{24})\text{SO}_4$ (Sokolova and Hawthorne, 2008 and references therein), depending on the availability of S. According to experimental data by Newton and Goldsmith (1977), end-member silvialite requires at least 775°C at 17kbar and 1200 °C at 10 kbar to form. Such conditions were confirmed by the study of Stolz (1987) whose pressure-temperature calculations indicated that silvialite from the McBride Province, North Queensland, Australia, crystallized from alkali basaltic magma at $\sim 900\text{--}1000^\circ$ and 8-12 kbar. This restricted stability field of meionite and silvialite scapolite means that those phases can be used to track C and S isotope signatures in the lower crust/upper mantle (e.g., Moecher et al., 1994; Yoshino et al., 2002; Hoefs et al., 1987; Iyver et al., 1992). For example, Moecher et al. (1994) studied C isotope signatures in scapolites from a range of deep crustal granulites and xenoliths, and concluded that these minerals derived their C primarily from a mantle source.

Studying the S isotope composition in scapolite from granulites is key to furthering our understanding of S recycling during high-grade metamorphism at convergent margins

(e.g., Alt et al., 2012; Evans et al., 2014, Tomkins and Evans, 2015; Evans and Powell, 2015). Moreover, Porter and Austrheim (2016) suggest that the breakdown of S-rich scapolite during retrogression of originally high temperature granulites might be a significant source for S in the middle/upper crust, as an important ligand for the transport of ore metals.

3. Samples and standard reference material (CB1)

3.1 Scapolite megacryst CB1 (Massif Central, France)

The Enval-Volvic volcanic line, east of the Chaîne des Puys in the Massif Central, France, is one of the few locations where S-rich scapolite megacrysts are found (Boivin and Camus, 1981). This 13 km long fissure is 90 kyr old, and represents one of the first volcanic episodes of the Chaîne des Puys, Massif Central, France. From south to north, the Enval-Volvic fissure is marked by the alignment of the Enval maar and the associated spatter cone of Chuquet-Genestoux; the Puy de Couleyras; the maar-spatter cone couples of Bois de Chanat and Bois de Clerzat; and the Puy de la Bannière above Volvic village. However, despite the current intraplate position of the Enval-Volvic volcanic line, several studies (e.g., Femenias et al., 2004 and references therein) found evidence that some xenoliths delivered by volcanics in the Massif Central record upper mantle metasomatism potentially related to earlier Variscan subduction.

Cobber 1 (CB1), sampled from the same location as given in Boivin and Camus (1981) is a large (~1 cm), euhedral scapolite crystal of a dark grey/green colour, hosted in tephra. In addition to scapolite, other megacrysts from the tephra include clinopyroxene + amphibole (kaersutite) + Fe-Ti oxides + feldspar (andesine to K-oligoclase) carried up by basalts erupted along the Enval-Volvic fissure (Boivin and Camus, 1981). Liotard et al. (1988 and references therein) suggest that the megacryst suite represents a paragenetic assemblage of phenocrysts that were in equilibrium with a differentiated, deep-seated magma.

3.2 Scapolite in mafic xenoliths from the Monaro Volcanic Province and Delegate Pipes, New South Wales (Australia)

We studied five scapolite-bearing granulites for which detailed petrological and petrographic descriptions, including EPM analyses can be found in Barrett (2014) (Fig. 3, and see appendix for sample location coordinates). The samples MVP99-2-05, MVP99-2-12, and MVP99-2-13 are xenoliths from the Eocene-Oligocene intraplate basaltic Monaro Volcanic Province (MVP) in New South Wales (NSW), southeastern Australia (Wellman and McDougall, 1974; Taylor et al., 1990; Roach, 2004). The MVP volcanic plugs and dykes, and less common maars, cover a range of primary to moderately evolved rocks, including: olivine nephelinite, melanephilinite, nepheline basanite, alkali olivine basalt, tephrite and K-trachybasalt (Roach, 2004). The more than 65 volcanic centers of the MVP delivered a variety of crustal and mantle xenoliths. The samples MVP99-2-12 and MVP99-2-13 represent garnet granulites with a mineral assemblage consisting of garnet ($\text{Al}_{35-37}\text{Gr}_{21-22}\text{Py}_{41-43}$) + clinopyroxene ($\text{En}_{38}\text{Fs}_{14}\text{Wo}_{48}$) + plagioclase ($\text{An}_{56-57}\text{Ab}_{40-41}\text{Or}_{2.8-2.9}$) + scapolite, as well as accessory rutile and magnetite. These samples have a coarse, equant texture with most of the grains being between 0.5 and 2 mm in diameter, forming a polygonal granular assemblage (Fig. 3). In sample MVP99-2-12, clinopyroxene is the most common mineral with an estimated modal abundance of ~40%, followed by plagioclase (~30%), garnet (~25%), and scapolite (~5%). Sample MVP99-2-13 contains clinopyroxene and garnet, both estimated at a modal abundance of ~35%, while plagioclase is estimated to make up ~25-30% of the mineral assemblage, and scapolite occurs as a minor phase (<5%). Garnet has distinct dark kelyphitic rims in both samples (Fig. 3), which have been interpreted to be a product of a breakdown reaction of garnet due to a sudden change of pressure and temperature when the xenoliths were transported to the surface (Keankeo et al., 2000). Scapolite shows conspicuous alteration rims that can vary from a few microns to ~20 microns thick. These fine-grained zones consist of a matrix of plagioclase and possibly sericite. Sample MVP99-2-05 is a two-pyroxene

granulite that contains an estimated modal abundance of ~35% plagioclase and clinopyroxene, ~25% orthopyroxene, and ~5–10% scapolite, which always shows alteration rims of similar composition to those observed in garnet-pyroxene granulite samples.

Sample 10438B also represents a two-pyroxene granulite collected from the Delegate breccia pipes, NSW, Australia, the same location where [Lovering and White \(1964\)](#) described for the first time S-rich scapolite in granulite xenoliths. The Delegate pipes are located approximately ~50km SW from the MVP samples described above. The major mineral phases (clinopyroxene ($\text{En}_{38}\text{Fs}_{12-14}\text{Wo}_{49}$)+orthopyroxene ($\text{En}_{65-67}\text{Fs}_{33-34}\text{Wo}_{0-1.5}$)+plagioclase ($\text{An}_{85-87}\text{Ab}_{13-15}\text{Or}_{0.2-0.3}$)+scapolite form a granular assemblage with sharp, polygonal grain boundaries ([Fig. 3](#)). Plagioclase is estimated to make up ~50% of the mineral assemblage, followed in abundance by ~30% orthopyroxene, and ~15% clinopyroxene. Scapolite occurs as a minor mineral phase (making up <5% of the mineral assemblage), and similar to the MVP samples, a reaction texture on the scapolite rims is always present ([Fig. 3F](#)). This sample shows compositional banding, defined by alternating pyroxene (orthopyroxene and clinopyroxene) and plagioclase-rich layers on both a hand specimen- and thin section-scale, interpreted as relict igneous cumulate layering.

Preliminary data from two-pyroxene granulites of the MVP by [Barrett \(2014\)](#) confirm earlier findings by ([Chen et al., 1998](#)) who dated two-pyroxene granulites from the nearby Delegate pipes. The work of [Chen et al. \(1998\)](#) revealed ages (U-Pb, zircon) of ~391 and ~398 Ma for the Delegate pipe granulites, confirming that these are significantly older than the volcanic activity at both localities (MVP: ~55–34 Ma; [Wellman and McDougall, 1974](#); Delegate pipes: ~170–160 Ma; [Lovering and Richards, 1964](#)). Based on experimental work on samples from the Delegate pipes, [Irving \(1974\)](#) concluded that the two-pyroxene xenoliths represent lower crustal material, whereas layered garnet-pyroxene xenoliths originally formed as cumulates in melt pockets in the mantle. [Barrett \(2014\)](#) and [White and Chappell \(1989\)](#) proposed that the two-pyroxene and garnet-pyroxene granulite xenoliths formed as igneous

cumulates with subsequent (re-)crystallization at granulite facies conditions in the lower crust. Granulite facies metamorphism in this part of Australia can be linked to the vast subduction-related accretionary orogenic system along the eastern Palaeo-pacific margin of Gondwana during the Palaeozoic and Mesozoic (Cawood and Buchan, 2007 and references therein).

3.3 Scapolite in granulite gneiss from the Shai Hill, south-east Ghana

We have also studied a scapolite-bearing gneissic granulite from the suture zone of the Dahomeyides orogen in south-east Ghana (sample MW1). This orogen is interpreted to have resulted from the easterly subduction of the rifted margin of the West African Craton during the Pan-African orogenic events (e.g., Affaton et al., 1991; Atttoh and Nude, 2008). The studied sample was collected from the high-grade metamorphic suture zone that comprises mafic-ultramafic rocks, eclogites, and granulite gneisses, which crop out in the Mampong Inselberg (Atttoh and Nude, 2008). MW1 comes from the same Shai Hill locality where Knorring and Kennedy (1958) originally described garnet-hornblende-pyroxene-scapolite gneiss. Peak metamorphism was likely attained at ~610 Ma when some of the suture zone rocks are thought to have reached mantle depths during a collisional orogeny at the West African Craton margin (Atttoh and Nude, 2008 and references therein). MW1 shows a distinct gneissic banding defined by garnet-pyroxene-hornblende and plagioclase-quartz rich zones. Scapolite is more abundant in the plagioclase bands, although it is still a minor mineral phase (<2%) when compared to garnet (~35%), plagioclase (~35%), clinopyroxene (~15%), and hornblende (~10). Rutile is the most common accessory mineral. Some scapolite grains are heavily altered (generally to K-feldspar), however, fresh scapolite occurs in the plagioclase-rich layers. These fresh scapolites do not contain a reaction rim as typically found in the other samples (see above).

4. Analytical methods

Matrix matched samples and reference materials are essential for SIMS analysis. Due to the potential for variable sputtering rates, crystallographic orientation of the standard and the unknown might also need to be matched or corrected for in some cases (e.g., Eiler et al., 1997). In order to test the homogeneity of natural scapolite, and to assess the effect of crystallographic orientation for S isotope analysis by SIMS, we chose a single scapolite megacryst from the Chaîne des Puys volcanics in the Massif Central, France (CB1, see above for sample description). After the inclusion-free scapolite crystal was freed from its surrounding tephra, sections were cut along the C- and A-axis, mounted in a 2.5 cm epoxy resin puck, and polished for microanalysis by EPMA, LA-ICP-MS and SIMS. Following EPMA mapping and LA-ICP-MS trace element analysis, we conducted SIMS S isotope traverses across the two fragments to test for homogeneity and crystallographic effects. EPMA and LA-ICP-MS analyses were conducted at the University of Western Australia, using a JEOL JXA8530F electron probe equipped with 5 tunable wavelength dispersive spectrometers and an Analyte G2 laser coupled to an X-series II mass spectrometer, respectively. Detailed information and the experimental set-ups for LA-ICP-MS and EPMA can be found in the electronic appendix.

Scapolite grains in the granulite samples were analysed in polished petrographic thin sections (~50-60 microns thick). Following imaging and EPMA analysis, small (2.5 mm) discs containing the targeted scapolite grains were extracted by microdrilling, and pressed into indium for SIMS and LA-ICP-MS analysis (see appendix for details).

4.1 Fluorination method

The S isotope composition of two aliquots of the same crystal were analysed by chemical extraction of total S, coupled with fluorination and dual-inlet gas-source isotope-ratio mass spectrometry in the Stable Isotope Laboratory of the Department of Earth and Planetary Sciences at McGill University. Sulfur from powdered fragments of CB1 was

extracted using a Kiba Reagent (Tin (II) Strong Phosphoric Acid; Kiba et al., 1955) technique as modified for samples with low S abundances (Hong et al., 2000). The Kiba reagent was prepared by heating a solution of 80.0g NaCl, 80.0g SnCl₂·2H₂O, and 1000g of orthophosphoric acid at 300°C until ≈190ml of liquid has evaporated from the mixture (Hong et al., 2000). A mixture of powdered CB1 and Kiba reagent was heated to 300°C, and held at this temperature for 60 minutes under a steady stream of N₂ gas. This liberated all S in the powder as H₂S, which was then bubbled through a 0.2 M AgNO₃ solution where it was precipitated directly as Ag₂S. The Ag₂S precipitate was collected, washed twice with doubly-deionized water, once with 1M ammonium hydroxide solution, twice again with doubly-deionized water, and then dried overnight. Dried Ag₂S samples were reacted with F_{2(g)} in nickel bombs at 250 °C to generate pure SF_{6(g)}. The isotopic composition of SF_{6(g)} was purified cryogenically and chromatographically and analyzed on a Thermo MAT-253 in dual inlet mode. Results were normalized to repeated measurements of international reference material IAEA-S-1, with a defined δ³⁴S value of -0.3‰ on the Vienna Canyon Diablo Troilite (V-CDT) scale. We took the δ³³S value of IAEA-S-1 to be -0.061‰ V-CDT and the δ³⁶S value of IAEA-S-1 to be -1.27‰ V-CDT (Wing and Farquhar, 2015). Sulfur isotope compositions are expressed as:

$$\delta^i\text{S} = \left(\frac{{}^iR_{\text{sample}}}{{}^iR_{\text{V-CDT}}} - 1 \right) \times 1000 \quad (1)$$

where ${}^iR = {}^i\text{S}/{}^{32}\text{S}$ and i is 3, 4, or 6, and

$$\Delta^j\text{S} = \delta^j\text{S} - 1000 \times \left(\left(1 + \frac{\delta^{34}\text{S}}{1000} \right)^{{}^j\lambda} - 1 \right) \quad (2)$$

where j is 3 or 6.

We calculated $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values through reference mass dependent exponents of ${}^{33}\lambda=0.515$ and ${}^{36}\lambda = 1.9$ (Wing and Farquhar, 2015). Uncertainty (2SD) on the entire

analytical procedure is estimated to be better than 0.3‰ for $\delta^{34}\text{S}$, 0.02‰ for $\Delta^{33}\text{S}$ and 0.3‰ for $\Delta^{36}\text{S}$.

4.2 SIMS

4.2.1 Analytical conditions

The SIMS analyses reported in this study were carried out using the Cameca IMS-1270 (#309) instrument at the School of GeoSciences at the University of Edinburgh, UK. Sulfur isotopes (^{32}S and ^{34}S) were analysed as S^- ions produced by bombardment of the target by a $\sim 5\text{nA}$, $^{133}\text{Cs}^+$ primary beam accelerated at +10kV, resulting in a net impact energy of 20keV at the sample surface. To eliminate charging during the analysis, the samples were coated with $\sim 30\text{nm}$ layer of gold and the exact position of the primary Caesium beam was flooded with low energy electrons produced by the normal incidence electron gun.

Secondary ions were accelerated at -10kV and analysed at a mass resolution of ~ 3600 , which is sufficient to resolve molecular interference by $^{16}\text{O}-^{18}\text{O}$, $^{33}\text{S}^1\text{H}$ and $^{32}\text{S}^1\text{H}_2$ on the $^{34}\text{S}^-$ peak. An energy window of 40 eV was used. After pre-sputtering for 60s, automated secondary ion beam alignment was performed using the DT_{xy} deflection plates to centre the beam in the mass spectrometer field aperture ($3,000\mu\text{m}$) and entrance slit ($80\mu\text{m}$) position. The L'2 and H'2 Faraday cups were calibrated at the start of each analytical session using in-built Cameca hardware and software.

Measurements of S isotopes were made simultaneously in multi-collection mode using two off-axis Faraday cups (L'2 for ^{32}S and H'2 for ^{34}S). Count rates were typically $\sim 9 \times 10^7$ cps of ^{32}S and $\sim 4 \times 10^6$ cps of ^{34}S . The total acquisition time was 160s comprising of 20 cycles, split into two blocks of 10, with each cycle comprising of a 8s counting period. A single ~ 5 -min analysis (including 60 s pre-sputtering time and beam centring routines) resulted in an internal error of $< 0.13\%$. Standards were analysed after every 10-15 unknowns so that the change in instrumental mass fractionation could be monitored and corrected for, if required.

4.2.2 Measurements

A total of 381 SIMS measurements were carried out over 4 different sessions, of which 224 measurements were of the reference scapolite CB1, fragments of which were mounted in each sample block. The scapolite reference CB1 had been previously checked for major element and isotopic homogeneity, together with confirmation that there was no preferential instrumental mass fractionation associated with crystal orientation (e.g., Kita et al., 2010).

Most sessions showed a slight linear drift in the instrumental fractionation with time, presumably caused by changes in the primary beam current and density. This linear drift was corrected for in each session by linear regression through the standard data acquired during that session. The correction for drift resulted in <0.1‰ correction to the data.

The average $^{33}\text{S}/^{34}\text{S}$ were calculated as cycles accumulated. Cycles outside the 3σ standard deviation were rejected. The remaining cycles were used to calculate the final $^{33}\text{S}/^{34}\text{S}$ and its standard deviation. This standard deviation divided by the square root of the number of retained cycles gives a standard mean error, referred to as internal precision (Fitzsimons et al., 2000). All unknown analyses were standardized with the S isotope values of CB1 obtained by the fluorination method.

5. Results

5.1 Major element concentrations of scapolites

Quantitative EPMA S maps of our standard scapolite CB1 show a subtle oscillatory growth zonation (Fig. 4). This difference can be detected by EPMA spot analyses where the difference in the S concentration between the bright zones (e.g., 3.9 wt.% SO_3 , Table 1) and the dark zones (e.g., 3.7 wt.% SO_3 , Table 1) is beyond the analytical uncertainty (~1.2 % at a 99% confidence level, see appendix Table). The average SO_3 content is 3.86 wt.% $\pm$ 0.15

(2SD) and $2.24 \text{ wt.\%} \pm 0.14 \text{ CO}_2$, while the average Cl concentration is $0.23 \text{ wt.\%} \pm 0.03$. The average Na_2O content is $3.80 \text{ wt.\%} \pm 0.22$, translating to a meionite component of $\sim 70\%$ (Table 1 and appendix).

Analyses of MW1 scapolite show uniform values for all major elements with SO_3 contents being close to $5 \text{ wt.\%}$ which equals to $XS \sim 0.57$, where XS is the atomic occupancy of S at the anion site (A) of the crystal defined as $A=1/(S+Cl+C)$ (e.g., Teertstra et al., 1999) (Table 1 and appendix). CO_2 fills the rest of the anion site, whereas Cl contents are negligible ($<0.1 \text{ wt.\%}$) (Table 1). This also agrees with quantitative EPMA element maps, which show a homogenous major element distribution and only subtle variations in S contents (Fig. 5). MW1 scapolite contains the highest Na_2O ($\sim 4.75 \text{ wt.\%}$) contents, which results in the lowest meionite component (Me% ~ 65).

Scapolite from the Delegate pipe locality (10438B) also contains $\sim 5 \text{ wt.\%}$ SO_3 and similar levels of calculated CO_2 ($\sim 1.9 \text{ wt.\%}$) as determined in MW1 ($\sim 2 \text{ wt.\%}$). However, the Na_2O content in 10438B scapolite is lower ($\sim 2.8 \text{ wt.\%}$) which results in a higher meionite component (Me% ~ 79.5). Some scapolite grains show S depletion and Cl and CO_2 enrichment towards the rim (SO_3 : $\sim 4.9 \text{ wt.\%}$ to $\sim 3 \text{ wt.\%}$, Cl: $\sim 0.01 \text{ wt.\%}$ to $\sim 0.02 \text{ wt.\%}$, and $\text{CO}_{2(\text{calc})}$: $2 \text{ wt.\%}$ to $3 \text{ wt.\%}$) (Fig. 5 and appendix table).

The scapolite compositions of MVP99-2-13 and MVP99-2-12 are homogeneous (Fig. 5, Table 1) and chemically similar, however, scapolite in MVP99-2-12 contains slightly higher SO_3 contents ($\sim 4.5 \text{ wt.\%}$) compared to MVP99-2-13 ($\sim 4.1 \text{ wt.\%}$). Scapolites from both samples contain similar amounts of CO_2 ($\sim 2\text{--}2.4 \text{ wt.\%}$), which means that similar proportions of S and C occupy the anion site (Table 1). MVP99-2-12 ($\sim 3.8 \text{ wt.\%}$) shows a minor enrichment in Na_2O relative to MVP99-2-13 ($\sim 3.4 \text{ wt.\%}$) whereby MVP99-2-12 has a lower meionite component ($\sim 70\%$) compared to MVP99-2-12 ($\sim 74\%$). Sample MVP99-2-05 contains the lowest average SO_3 concentrations ($\sim 3.3 \text{ wt.\%}$), which means that CO_2 is the major volatile component in the crystal structure ($XC \sim 0.6$). The Na_2O content of MVP99-2-

05 is ~2.9 wt.% (Me ~77%) (Table 1). Some of the scapolites show zoned S concentrations, which are mirrored by Cl and CO_{2(calcd)} contents, where cores have higher S contents (~4.4 wt.% SO₃) than rims (~3.3 wt.% SO₃). Chlorine can be slightly enriched in rims (~0.05 wt.%) compared to cores (~0.03 wt.%), which is also true for CO_{2(calcd)} (~2.2 wt.% in core vs. ~2.8 wt.% in rim) (Fig. 5, appendix table and Fig. A-1). K₂O concentrations for all the analysed samples are low (<0.3 wt.%) and FeO and MgO are typically <0.5 wt.%.

5.2 Trace element concentrations LA-ICP-MS

The complete data set for trace elements measured via LA-ICP-MS can be found in the appendix. Scapolites may contain several tens of ppm LREE, whereas HREE concentrations are in the sub-ppm range. Beside sample MW1, which only shows a subtle positive Eu anomaly, all studied scapolites show a distinct positive Eu anomaly and HREE depleted chondrite-normalized trace element patterns (Fig. 6). Scapolites in garnet-bearing granulites are more depleted in HREE than the two-pyroxene granulites and CB1, with Er, Yb, and Lu concentrations often being below the limit of detection. While no trace element variations within individual grains and samples are observed, scapolite from different samples contain variable concentrations of Sr, Ba and Pb (see appendix). For instance, scapolite in samples CB1 and MVP99-2-12 contain ~2000–2400 ppm Sr on average, while sample 10438B contains ~500 ppm Sr. Similarly, Ba contents in scapolite from sample 10438B (~30 ppm) are lower compared to Ba concentrations in MVP99-2-12 and CB1 (~70 ppm and ~125 ppm, respectively). Lead values are highest in sample MW1 (~5.3 ppm on average) and lowest in CB1 (~1.1 ppm).

5.3 Fluorination method

The two repeats of the CB1 aliquots are consistent within analytical uncertainty and give $\delta^{34}\text{S}$ values of $5.22\text{‰} \pm 0.30$ (2SD) and $4.94\text{‰} \pm 0.30$ (2SD), with mass-dependent

$\Delta^{33}\text{S}$ ($-0.008\text{‰} \pm 0.016$; $-0.018\text{‰} \pm 0.016$) and $\Delta^{36}\text{S}$ values ($-0.21\text{‰} \pm 0.30$; $-0.28\text{‰} \pm 0.30$). Uncertainties in the $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values for CB1 covary strongly with the uncertainties for $\delta^{34}\text{S}$ values due to mass-dependent fractionation processes in the measurement procedure (cf. Wing and Farquhar, 2015), giving rise to significant statistical covariances among the uncertainties in these measurements (see appendix).

5.4 S isotope analysis by SIMS

5.4.1 CB1 as primary calibration standard for in situ S isotope analysis

The existence of S-rich scapolite has been known for several decades. Until now, however, in situ methods for S isotope analysis in scapolite have not been applied, due mainly to the scarcity of potential standard reference material and unknown crystallographic effects for SIMS analysis. We found that the $^{34}\text{S}/^{32}\text{S}$ ratio of CB1 measured by SIMS is independent of the crystallographic orientation of the systematically analysed scapolite fragments and of the oscillatory zonation in this crystal (Fig. 7). The concentration of S, which can semi-quantitatively be monitored by the ^{34}S counts, is independent of the $^{34}\text{S}/^{32}\text{S}$ ratio (See appendix Fig. A-2). The reproducibility of $\delta^{34}\text{S}$ values in CB1 over four analytical sessions is 0.40‰ (2SD), comparable to the reproducibility of the two bulk-grain aliquots analysed by the fluorination method (see above). These data, coupled with elemental homogeneity and the lack of inclusions make CB1 suitable as a primary calibration standard for S isotope analyses by SIMS. Furthermore, the chemical composition of CB1 (Table 1) falls within the range of all unknowns, which minimises the potential for analytical matrix effects. Scapolite CB1 was subsequently used to standardize all the SIMS analyses of the unknown scapolite from the granulite samples (see below).

5.4.2 Sulfur isotope analysis in scapolite from granulites

Scapolite grains from sample MVP99-2-05 (two-pyroxene granulite) are internally homogeneous for $^{34}\text{S}/^{32}\text{S}$, however, $\delta^{34}\text{S}$ values vary from -0.9 to +0.3 between individual grains within the same thin section (Fig. 8). The second two-pyroxene granulite sample, 10438B, shows a homogeneous S isotope pattern of individual grains with a mean $\delta^{34}\text{S}$ value of 0.07 ± 0.16 (2SD) ‰. As with sample MVP99-2-05, scapolite of MVP99-2-12 (garnet granulite) shows S isotope differences between individual grains. The highest S isotope ratios measured in this sample are approximately +3 ‰ $\delta^{34}\text{S}$, whereas the lowest S isotope ratios are $\sim +1.7$ ‰ $\delta^{34}\text{S}$ (Fig. 8). Importantly, scapolites from this sample are chemically homogeneous without S depletion towards the rims (Fig. 5). The other garnet-granulite sample, MVP99-2-13, contains scapolite with a homogeneous S isotope composition of $+1.25 \pm 0.17$ ‰ $\delta^{34}\text{S}$. Scapolites from sample MW1, representing the garnet-pyroxene-hornblende granulite from Mampong, Shai Hills, southeastern Ghana, also show a homogeneous (relative to analytical reproducibility) S isotope composition of $+4.22 \pm 0.37$ ‰ $\delta^{34}\text{S}$ with no resolvable variations between the analysed grains.

In general, scapolite from the garnet bearing samples has elevated $\delta^{34}\text{S}$ values compared to scapolite of the two-pyroxene granulites MVP99-2-05 and 10438B (Fig. 8). However, CB1 scapolite, part of a garnet-absent assemblage, contains the heaviest S isotope signature ($\sim +5.08$ ‰ $\delta^{34}\text{S}$, see section 5.3).

6. Discussion

6.1 Formation conditions of the studied scapolites

The high-resolution quantitative EPMA maps show a subtle but distinct oscillatory growth pattern in CB1 (Fig. 4), which under the assumed P-T formation conditions supports an igneous origin. HREE abundances of CB1 follow the same pattern as scapolite from garnet-absent granulites (Fig. 6 and see below), which suggests the absence of garnet in the

source and agrees with the lack of garnet megacrysts in the host basaltic tephra. The formation of scapolite megacrysts in the Chaîne des Puys has previously been explained by a high $f\text{SO}_2$ content and exceptionally high $f\text{O}_2$ in the relatively undifferentiated alkalic magma source (Boivin and Camus, 1981). Boivin and Camus (1981) concluded that the megacrysts formed at high pressure and temperature (~ 10 kbar and $\sim 1100^\circ\text{C}$) from a basic magma under high $a\text{H}_2\text{O}$ conditions.

Irving (1974) performed experiments on two-pyroxene and garnet-plagioclase-pyroxene granulite xenoliths from the Delegate pipe locality. The experiments showed that the mineral assemblage, although scapolite-deficient, can be reproduced at 6-10 kb and 1100°C for two-pyroxene granulites. Garnet pyroxenite xenolith assemblages were reproduced at 13-17 kbar and ~ 1050 to 1100°C . The samples studied here are very similar to those described in Irving (1974). Barrett (2014) studied MVP and Delegate pipe xenoliths in detail and estimated pressure-temperature conditions of ~ 11 kbar and $\sim 1050^\circ\text{C}$ for a scapolite-bearing garnet granulite (MVP99-2-12). Calculations for the P-T conditions of two-pyroxene granulites also support the previously constrained P-T formation environment by Irving (1974). Barrett (2014) concluded that (scapolite-bearing) granulites from NSW (Australia) likely represent cumulates that recrystallized under granulite facies conditions, which agrees with earlier findings by Irving (1974) and White and Chappell (1989). A cumulate origin for these samples is supported by the distinct banding of garnet, pyroxene, and plagioclase-layers and the conspicuous positive Eu anomalies evident in whole-rock analyses.

Thermobarometric calculations on garnet-bearing granulites from the Dahomeyide suture zone (sample MW1) suggest a peak metamorphic temperature of at least $\sim 800^\circ\text{C}$ and ~ 13 – 14 kbar for samples from the Shai Hill locality (Attoh and Nude 2008 and references therein). The presence of primary hornblende supports lower formation temperatures than reported for the other studied scapolite-bearing samples.

Chondrite normalized trace element patterns of scapolite from garnet-bearing and garnet-absent samples are distinctly different (Fig. 6). Scapolites in garnet-bearing samples are more depleted in HREE than their equivalents in garnet-absent granulites. This strongly suggests preferential HREE partitioning into garnet at the time of scapolite formation, resulting in a more prominent HREE depletion in the coexisting scapolite (cf. Hammerli et al., 2014). Based on this, together with textural relationships and polygonal grain boundaries, we infer that scapolite in the studied granulites formed at peak metamorphic conditions, when the major mineral phases crystallized together.

6.2 Major element composition of scapolites

Whereas scapolite grains from samples MVP99-2-12, MVP99-2-13 and MW1 are homogeneous in terms of their major element composition, some scapolite in granulite xenoliths 10438B and MVP99-2-05 show S, Cl, and CO₂ compositional zonation. The replacement of S-rich scapolite by more C- and Cl-rich scapolite, possibly via dissolution-recrystallization (see Putnis and Austrheim, 2010), has been observed in retrogressed scapolite (Porter and Austrheim, 2016). In the samples of the present study, the substitution of Cl for S along cracks further supports retrogressive processes rather than changing physiochemical conditions during the mineral's formation.

6.3 Scapolite formation and the source of S

Meaningful interpretation of S isotope data from high-grade rocks is challenged by the possibility of multiple generations of sulfide formation, and subsequent S mobility during retrograde metamorphism and/or alteration at low temperatures (e.g., Morrison and Valley, 1991). In the studied samples, scapolite is the only S-bearing phase, and due to its restricted stability field (see above) it is likely that scapolite records the local S isotope signature present at the time of its formation in the lower crust.

527 Interestingly, some samples (MVP99-2-05 and MVP99-2-12) show isotope variations
528 on an intra-sample-scale beyond the analytical uncertainty (Fig. 8). We interpret this as
529 evidence for isotope heterogeneity of the local S source within the sample (discussed below).

530 All samples, except CB1, are inferred to be associated with a convergent margin
531 setting, where granulite facies conditions were reached in deep arc lithosphere. There are four
532 possible scenarios for the origin of the S sequestered by scapolite in granulites: A)
533 sedimentary S-bearing phases (sulfides, sulfates) react to scapolite during high-T
534 metamorphism; B) scapolite crystallizes as a primary igneous phase, C) scapolite receives its
535 S component and isotope signature from an external fluid during high-grade metamorphism
536 and D) primary magmatic S-bearing phases supply S for scapolite formation during the (re-
537)crystallization of the magmatic mineral assemblage under granulite facies conditions.
538 Scenario A can be ruled out for CB1 and also for the NSW samples given the evidence that
539 granulites from the Delegate breccia pipes and MVP represent recrystallized igneous
540 cumulates (see section 5.1); we cannot, however, exclude the possibility that the protolith to
541 sample MW1 had a prior upper crustal history. [Stolz \(1987\)](#) studied scapolite in mafic
542 xenoliths from the McBride Province, Australia. He found idioblastic scapolite inclusions in
543 plagioclase and clinopyroxene as well as garnet reaction coronas around scapolite grains.
544 Together with the compositional banding and P-T calculations, [Stolz \(1987\)](#) suggested that
545 scapolite crystallized as a primary magmatic phase to subsequently form igneous cumulates.
546 Despite some similarities to the McBride xenolith samples (e.g., compositional banding), the
547 absence of scapolite inclusions in other co-existing minerals argues against the scapolite
548 grains in the present study forming by direct igneous crystallisation (scenario B). We found
549 no obvious evidence for the infiltration of external S-rich fluids (scenario C) such as
550 scapolite-rich veins, as for example seen in some deep-seated gabbros of the Kohistan Arc
551 ([Yoshino and Satish-Kumar, 2001](#)) or the Bergen Arcs region of Western Norway (Porter and
552 Austrheim, 2016). In the studied samples, scapolite is not restricted to certain zones, but

rather homogeneously distributed in the sample and in textural equilibrium with garnet and pyroxene. Furthermore, the mineralogy of the scapolite-bearing granulites suggests a “dry” environment for their formation, hence, the putative fluid would have been H₂O-deficient.

Scenario D, scapolite formation with S derived from reactions with primary magmatic sulfides, seems the most feasible process. It is generally agreed that the formation of S-rich scapolite requires oxidised conditions (Boivin and Camus, 1981; Stolz, 1987), which can be achieved by the infiltration of oxidizing fluids. However, Goldsmith (1976) proposed a simplified reaction between sulfides, oxides and silicates, where oxidation takes place via a ferrous-ferric equilibrium with primary high-T deep crustal minerals:

If this reaction takes place, Goldsmith (1976) proposes that no oxygen transfer or other oxidizing agents (e.g., fluid) are required to form scapolite. However, fluxing of the lower crust by CO₂ exsolved from underlying crystallizing magmas (see Moecher et al., 1994), might play an important role in facilitating the above reaction. This is because such a process further stabilizes melonitic scapolite over other phases at high P and T (Goldsmith and Newton, 1977), thereby driving the reaction to the right and augmenting (re-)crystallization of the primary (igneous) mineral assemblage under granulite facies conditions (Harlov, 2012 and references therein). The presence of Fe-oxides with scapolite as observed in thin sections supports scapolite formation via the above reaction. Such processes would also explain the rather homogeneous scapolite distribution in the studied samples. Further support for the importance of the coupled redox reaction between ferrous/ferric Fe and sulfate/sulphide comes from the reversed process inferred by Porter and Austrheim (2016). These authors suggest that scapolite sulfate is reduced to sulphide during scapolite retrogression by the oxidation of ferrous Fe in the bulk rock and simultaneous formation of ferric minerals. In our samples, the absence of other S-bearing minerals besides scapolite, and provided that S was not introduced from an external source, could suggest that primary sulfides were the limiting

reaction agent, whereas as the other components (magnetite and Fe-bearing silicates, such as garnet and pyroxene), and potentially externally-derived CO₂ were present in excess. This would imply that the vast majority of S accumulated in the lower crust became subsequently recycled into scapolite. Isotopic fractionation of S would not be expected in this scenario, as supported by the narrow range of S isotope ratios within most samples and the absence of isotopic zonation within individual grains (but see below).

6.4. Isotope variability on a sample-scale

There are multiple possible causes for the observed S isotope variation within samples MVP99-2-12 and MVP99-2-05 (Fig. 8). It is possible that in- or out-diffusion on a mineral scale was variable within the sample. However, S isotope profiles through scapolite grains do not reveal any evidence for diffusion, such as e.g. systematic intragrain variations. We therefore regard diffusion as having a minor effect on the S isotope variation. In the case of MVP99-2-05 it could be argued that retrogression (i.e. the localised replacement of S by Cl) led to different isotope signatures in scapolite from grain to grain. This explanation cannot, however, apply to scapolite of sample MVP99-2-12, which lacks compositional zoning or localised Cl enrichment (Fig. 8).

Previous in situ S isotope studies on mantle rocks have also found within-sample $\delta^{34}\text{S}$ variations of several permil, as well as intra-grain variations outside of analytical uncertainty (e.g. Chaussidon et al., 1989, Giuliani et al., 2016). One explanation for the isotope variability observed in the latter study might be the incomplete isotope homogenization of monosulfide solid solution minerals during their equilibration at relatively low temperatures ($\sim 600^\circ\text{C}$) (Giuliani et al., 2016 and references therein). Chaussidon et al. (1989) observed S isotope variation in sulfide globules hosted in pyroxene from pyroxenite cumulates. The authors interpret the isotope variations between sulfide globules to be a direct result of mantle S isotope heterogeneity caused by migrating fluids in the mantle, which may have carried

different S-bearing species with variable S isotope signatures. Conceivably, such initial isotope variations of primary magmatic sulfides, as reported by Chaussidon et al. (1989), are mirrored in scapolite that subsequently formed by replacement of sulfide globules during high-grade granulite facies metamorphism, in the presence or absence of an oxidizing fluid.

Despite the homogeneous spatial distribution of scapolite and the sample-scale isotope heterogeneities, we cannot entirely exclude S addition to the system by percolating mantle-derived fluids. This alternative scenario of an external S-source (as described by Austrheim, 2013), would, however, require an isotopically heterogeneous fluid, at least on a sample scale, to form the observed S isotope heterogeneities between individual scapolite grains.

6.5. Sulfur isotope signatures in scapolite and their implications for S in the lower crust

There is evidence that parts of the mantle underwent metasomatism, which is reflected by distinct S isotope signatures of metasomatized peridotite samples (e.g., Wilson et al., 1996; Giuliani et al., 2016, Fig. 9). However, the length scale of mantle metasomatism is difficult to constrain, and it is unclear if metasomatized material, including fluids, might be introduced into the lower crust. The measured S isotope signatures of scapolites from the studied granulites fall within the range of S isotope ratios typically found in unaltered mantle rocks (Fig. 9). Based on the initial sample set targeted here, there is no evidence that S-bearing fluids sourced directly from subducted sediments (e.g., seawater sulfate) control scapolite formation in the lower crust. If this were the case, $\delta^{34}\text{S}$ signatures of scapolite would be expected to be significantly heavier ($>>5\text{‰ } \delta^{34}\text{S}$). It is possible, however, that the S isotope signature of slab-derived fluid was diluted and camouflaged by interaction with the sub-arc mantle prior to percolating into the lower crust.

While we cannot exclude the possibility that slab-derived fluid interacted with the sub-arc mantle, our results, together with those of previous studies show that the S isotope signatures of granulites and pristine mantle rocks are indistinguishable (Figs. 2, 9). This

observation is in accordance with Moecher et al.'s (1994) findings that lower crustal scapolite acquires C from a mantle source, and challenges the concept that slab-derived fluids play a key role in universally enriching arc magmas in ^{34}S . These findings might be further tested by studying the S isotope signatures of scapolites from deep crustal samples of other arc terranes.

6.6 Scapolite as a S source in the middle crust

Porter and Austrheim (2016) recently found that S-rich scapolite formed in lower crustal granulites becomes unstable during hydration and deformation at amphibolite facies conditions. Release of S from the breakdown of scapolite can lead to the formation of sulfides in the reaction zone, which might subsequently be mobilized by further hydration or deformation. Lovering and White (1964) determined that the scapolite reaction rims in samples from the Delegate pipes consist of very fine-grained plagioclase. We found that these scapolite reaction zones are typically associated with elevated K concentrations. The lack of secondary sulfides in the reaction zones of scapolite suggests that S was fully mobilized after peak-metamorphic scapolite breakdown (see also Porter and Austrheim, 2016). Scapolite retrogression at mid-crust levels therefore likely contributes significant S to the overall S budget, where the composition of the percolating fluids would be crucial for the transport of this liberated S (Porter and Austrheim, 2016). This process is potentially of key importance for the mobilization and concentration of chalcophile ore elements in the surrounding crust.

7. Conclusions

We characterized an isotopically homogeneous S-rich scapolite (CB1), suitable as a primary calibration standard for in situ SIMS analysis. SIMS S isotope analysis in scapolite is independent of crystallographic orientation.

EPMA maps of the CB1 megacryst show oscillatory growth zonation, typical for the formation of igneous minerals. This supports earlier findings of an igneous origin of scapolite

megacrysts from the Chaîne de Puys. The elevated $\delta^{34}\text{S}$ ($\sim +5\text{‰}$) values of CB1 indicate that the mantle source for intraplate volcanic activity in the Chaîne de Puys contains a heavy S isotope reservoir. Given the geodynamic setting, this reservoir is not directly associated with coeval subduction processes, which is also supported by the mantle-like $\delta^{13}\text{C}$ signature of scapolite from the same location (Moecher et al., 1994). This suggests that the upper mantle can in some cases be a reservoir of relatively heavy S, which in this case potentially represents a memory effect of heavy S from previous Variscan subduction in the region (Femenias et al., 2004).

Sulfur isotope signatures from lower crustal rocks represented by garnet-pyroxene and two-pyroxene granulites from eastern Australia and south-eastern Ghana, both associated with convergent tectonics, plot between ~ -0.5 and $\sim +4\text{‰}$ $\delta^{34}\text{S}$. Sulfur isotope ratios of these samples fall within the range of S isotope signatures reported from mantle rocks. These results therefore provide no evidence for a major seawater component (i.e. slab-derived fluids) in the lower crust beneath these areas, which we anticipate would lead to $\delta^{34}\text{S}$ values of $\gg +4\text{‰}$.

Our preferred model for S isotope variations in some of the studied samples involves the presence of isotopically heterogeneous magmatic S-phases prior to metamorphism. This would require that the initial magmas from which the primary S-phases separated were not isotopically homogeneous. Isotope heterogeneity of mantle melt, as preserved in scapolite, could be due to the melting of different mantle source domains, or to the local interaction of mantle peridotite with externally-derived fluids. However, the putative external fluid flux in this scenario was evidently insufficient to shift the S isotope signature of the source peridotite away from the established mantle range. Subsequent granulite facies metamorphism of mantle cumulates likely took place under relatively dry conditions (i.e. low fluid/rock ratios) as local S isotope variations prevail.

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Figure/Table captions

Figure 1: Simplified sketch of hypothesised S recycling in subduction systems with references to key studies of the respective reservoirs. Examples for S isotopes studies in lower crustal rocks (granulites and cumulates) include Hoefs et al. (1987) and Iyver et al. (1992). The dotted box represents the mantle-crust interface, for which comprehensive datasets are lacking.

Figure 2: Compilation of S isotope signatures (compared to VCDT) in different reservoirs.

Figure 3: Scans of polished thin sections of the studied scapolite-bearing granulite samples. MVP99-2-13 (A), MVP99-2-12 (B) and MW1 (C) are garnet-pyroxene-(hornblende) granulites. MVP99-2-05 (D) and 10438B (E, F) are two-pyroxene granulites. F) Microphotograph in plane-polarized light of sample 10438B, where the white arrows point to

the alteration rims of scapolite. Opx=orthopyroxene, Scp=scapolite, Pl=plagioclase;
Cpx=clinopyroxene; Grt=garnet.

Figure 4: Quantitative S map of CB1. The larger upper piece represents the A-plane
(perpendicular to the A-axis) and the smaller lower piece represents the C-plane (a slice along
the C-axis) of the crystal. Stereonets show the poles for each crystal plane, plotted relative to
the 001 plane.

Figure 5. Quantitative EPMA S maps of representative scapolite grains. Scapolite grains
from sample MVP99-2-12 and MVP99-2-13 show homogeneous S concentrations in
individual grains. Scapolite in sample MVP99-2-05 and 10438B show S depletion towards
their rims. The mapped scapolite grain from sample MW1 shows an irregular S distribution
without distinct core-rim correlations.

Figure 6: Chondrite normalized (McDonough and Sun, 1995) REE analyses of scapolite by
LA-ICP-MS.

Figure 7: Reproducibility of S isotope measurements from scapolite CB1, as assessed by 224
individual SIMS analyses, where the measured $^{34}\text{S}/^{32}\text{S}$ ratios are normalised to the whole
grain $\delta^{34}\text{S}$ value of CB1 (+5.08 ‰). The weighted mean value is shown as the black
horizontal line. Black bars represent analyses from a traverse perpendicular to the C-axis of
CB1 (average $\delta^{34}\text{S}$ = +4.91 ‰ ± 0.44 (2SD)), dark grey bars represent measurements from a
traverse perpendicular to the A-axis (average $\delta^{34}\text{S}$ = +5.08 ‰ ± 0.41 (2SD)), and light grey
bars represent the combined analyses over 4 analytical sessions on various CB1 crystal
fragments (average $\delta^{34}\text{S}$ = +5.05 ‰ ± 0.41 (2SD)). All data points include 2SD uncertainties,

which combine in-run (measured) uncertainties and the uncertainty of the bulk grain reference values, summed in quadrature.

Figure 8: Average S isotope composition of individual scapolite grains of the studied samples. Error bars represent 2SD.

Figure 9: Comparison of S isotope signatures of lower crustal rocks (Hoefs et al., 1981; Ivyer et al., 1992), mantle-rocks (Ionov et al., 1992; Wilson et al., 1996), and S isotope analysis in scapolite from granulites (error bars are 2SD). The S isotope variation in Ionov et al. (1992) might be a result of isotope fractionation due to melt extraction (e.g., Chaussidon et al., 1989).

*presence of secondary scapolite, **metasomatized.

Table 1: Representative EPMA data of scapolite for each studied sample. The number of ions is calculated on the basis of 12 (Si, Al). CO₂ is calculated on the assumption that the T space is fully occupied by C, S and Cl, hence $C=1-S-Cl$. Meionite equivalent% is expressed as $Me\% = 100[\sum(\text{divalent cations})/4]$ and equivalent anorthite content as $EqAn = 100(Al-3)/3$. CB1(bright) and CB1(dark) refer to the bright and dark zonation shown in Fig. 4.

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Figure 1

Figure 2

Marine sulfates/sedimentary pyrite: Farquhar et al. (2010) and therein. *OIBs:* Sakai et al. (1984); Torssander (1989); Chaussidon et al. (1989); Cabral et al. (2013). *MORBs:* Kanehira et al. (1973); Sakai et al. (1984); Labidi et al. (2012, 2013). *Mantle xenoliths:* Chaussidon et al. (1989); Chaussidon & Lorand (1990); Kyser (1990); Ionov et al. (1992); Wilson et al. (1996). *Arc Volcanics:* Ueda & Sakai (1984); Alt et al. (1993); Woodhead et al. (1987); de Hoog et al. (2001), Marini et al. (2011). *Continental tholeiites:* Schneider et al. (1970). *Continental alkali-rich rocks:* Schneider et al. (1970), Harmon et al. (1987)

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1

Sample	10438B	MVP99-2-13	MVP99-2-05	MVP99-2-12	MW1	CB1(bright)	CB1(dark)	CB1 (n=16)	
(wt.%)								average	2SD
SiO ₂	43.85	46.15	44.59	46.52	47.66	44.97	45.59	45.48	0.60
Al ₂ O ₃	27.63	26.37	27.93	26.00	25.43	27.24	26.78	26.16	1.03
FeO	0.26	0.33	0.24	0.39	0.19	0.35	0.42	0.43	0.13
CaO	18.55	16.89	18.40	16.02	15.46	16.89	16.64	16.57	0.26
MgO	0.17	0.49	0.22	0.44	0.07	0.09	0.09	0.09	0.02
Na ₂ O	2.70	3.41	2.99	3.84	4.76	3.85	4.07	3.80	0.23
K ₂ O	0.06	0.13	0.12	0.20	0.07	0.24	0.22	0.23	0.05
Cl	0.01	0.03	0.04	0.07	0.05	0.20	0.24	0.23	0.03
SO ₃	5.09	4.13	3.28	4.58	4.92	3.96	3.73	3.86	0.15
CO ₂ (calc)	1.85	2.40	2.88	2.11	1.98	2.27	2.36	2.24	0.14
Total	100.18	100.33	100.68	100.16	100.59	100.08	100.14	99.11	1.65
–O=Cl	0.00	0.01	0.01	0.02	0.01	0.05	0.05	0.05	0.01
Total Cl corrected	100.18	100.32	100.67	100.14	100.58	100.03	100.08	99.06	1.66
Total (12/Si+Al)	9.43	9.34	9.30	9.34	9.29	9.35	9.34		
Si	6.89	7.17	6.90	7.23	7.37	7.00	7.09		
Al	5.11	4.83	5.10	4.77	4.63	5.00	4.91		
Fe	0.03	0.04	0.03	0.05	0.02	0.05	0.05		
Ca	3.12	2.81	3.05	2.67	2.56	2.82	2.77		
Mg	0.04	0.11	0.05	0.10	0.02	0.02	0.02		
Na	0.82	1.03	0.90	1.16	1.43	1.16	1.23		
K	0.01	0.03	0.02	0.04	0.01	0.05	0.04		
Cl	0.00	0.01	0.01	0.02	0.01	0.05	0.06		
S	0.60	0.48	0.38	0.53	0.57	0.46	0.43		
C	0.40	0.51	0.61	0.45	0.42	0.48	0.50		
Me%	79.30	73.83	77.27	70.20	64.35	70.45	69.16		
EqAn#	70.48	60.99	69.90	58.90	54.47	66.66	63.67		
XS	0.6	0.48	0.38	0.53	0.57	0.46	0.43		
XC	0.4	0.51	0.61	0.45	0.42	0.48	0.50		