Sulfur isotope composition of metasomatised mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa): ~~problems, solutions, implications~~contribution from subducted sediments and the effect of sulfide alteration on S isotope systematics

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Abstract

Sulfur isotopes are a powerful geochemical tracer in high-temperature processes, but have rarely been applied to the study of mantle metasomatism. In addition, there are very limited S isotope data on sub-continental lithospheric mantle (SCLM) material. For cratonic regions, these data are restricted to sulfide inclusions in diamonds. To provide new constraints on the S isotope composition of the SCLM and on the source(s) of mantle metasomatic fluids beneath the diamondiferous Kimberley region (South Africa), we investigated the S isotope systematics of five metasomatised mantle xenoliths from the Bultfontein kimberlite. Pentlandite and chalcopyrite in these xenoliths were analysed by *in situ* secondary-ion mass spectrometry (SIMS), with bulk-rock material measured by gas source isotope ratio mass spectrometry techniques. Based on previous studies, the xenoliths experienced different types of metasomatism to one another at distinct times (~180 and ~90-80 Ma). Contained ~~sulfide-pentlandite~~ grains show variable alteration to heazlewoodite (i.e. Ni sulfide) + magnetite. The *in situ* S isotope analyses of pentlandite exhibit a relatively restricted

range between -65.9 and -1.4% $\delta^{34}\text{S}$ (compared to VCDT), with no statistically meaningful differences between samples. Chalcopyrite only occurs in one sample and shows $\delta^{34}\text{S}$ values between -625.4 and -1.0% . The bulk-rock S_{sulfide} isotope analyses vary between -3.4 and $+0.8\%$ $\delta^{34}\text{S}$. Importantly, the only sample hosting dominantly fresh sulfides shows a bulk-rock $\delta^{34}\text{S}$ value consistent with the mean value for the sulfides, whereas the other samples exhibit higher bulk $^{34}\text{S}/^{32}\text{S}$ ratios. The differences between bulk-rock and average *in situ* $\delta^{34}\text{S}$ values are directly correlated with the degree of sulfide alteration. This evidence indicates that the elevated $^{34}\text{S}/^{32}\text{S}$ ratios in the bulk samples are not due to the introduction of heavy S (commonly as sulfates) and are best explained by isotopic fractionation coupled with the removal of light S during serpentinisation, when pentlandite is altered to S-poor mixtures of heazlewoodite and magnetite. Available bulk S_{sulfide} isotopic data for SCLM peridotite xenoliths are dominated by positive $\delta^{34}\text{S}$ values, which contrasts with the negative values of the sulfides. These results imply that the mantle S isotope values from bulk peridotite samples are commonly modified by isotopic fractionation during serpentinisation. Therefore, the S isotopic composition of the SCLM may require revision. The limited isotopic variability shown by sulfides in the Bultfontein mantle xenoliths is probably due to intermittent tapping of a mantle source with a relatively homogeneous-restricted S isotope composition. While the asthenospheric mantle ($\delta^{34}\text{S} \leq -1.4\%$) is a viable candidate, $\delta^{34}\text{S}$ values as low as -65.9% require input from recycled crustal material, possibly represented by the sulfur reservoir with negative $\delta^{34}\text{S}$ signature that is missing in the >500 Ma sedimentary record and could have been subducted and stored in the Earth's mantle.

Keywords: sulfur isotopes; sulfides; mantle xenoliths; Kimberley; SIMS

1. Introduction

Sulfur isotopes provide an excellent geochemical tracer of high-temperature mantle processes, due to minimal isotope fractionation at high temperature (e.g., Ohmoto and Rye, 1979; Marini et al., 2011), unless redox reactions are involved, and large differences between mantle and crustal reservoirs (Fig. 1). Sulfur isotope ratios are not affected by partial melting or sulfide crystallisation from sulfide or silicate melts (Ohmoto and Rye, 1979; Marini et al., 2011). Sulfur isotope values for mantle-derived rocks, minerals and magmas that deviate significantly from $\delta^{34}\text{S}$ of 0‰ (compared to the Vienna Canon Diablo Troilite (VCDT) reference material) are commonly interpreted to reflect contributions of surface-derived S recycled into the Earth's mantle via subduction at convergent margins (e.g., Chaussidon et al., 1987; de Hoog et al., 2001; Eldridge et al., 1991; Ionov et al., 1992; Labidi et al., 2013, 2014, 2015; Thomassot et al., 2009; Wilson et al., 1996).

The discovery that extensive mass independent fractionation of S isotopes (expressed as ‰ $\Delta^{33}\text{S}$ variations compared to VCDT) only occurred until ~2.4 Ga (Farquhar and Wing, 2003 and references therein) has provided an additional tool to trace the incorporation of ancient recycled crustal S in the mantle. Studies of sulfide inclusions in diamonds (Farquhar et al., 2002; Thomassot et al., 2009) and olivine from ocean island basalts (Cabral et al., 2013) have demonstrated that mass-independent fractionated S can be preserved in the Earth's mantle.

Surprisingly, S isotope geochemistry has only been applied to genetic studies of metasomatic melts/fluids in the mantle on rare occasions (Chaussidon and Lorand, 1990; Ionov et al., 1992; Wilson et al., 1996). Ionov et al. (1992) and Wilson et al.

(1996) attributed high $^{34}\text{S}/^{32}\text{S}$ ratios of bulk peridotite xenoliths from central Asia and Dish Hill (California), respectively, to metasomatism by slab-derived fluids. Chaussidon and Lorand (1990) suggested that high $\delta^{34}\text{S}$ values from sulfide grains in orogenic peridotites from the Pyrenees (France) indicate the occurrence of recycled oceanic crust in the mantle source of the metasomatic melts. Conversely, metasomatism by asthenospheric fluids was advocated for Dish Hill mantle xenoliths with circa-chondritic bulk $\delta^{34}\text{S}$ values (Wilson et al., 1996).

The S isotope composition of the sub-continental lithospheric mantle (SCLM) is also poorly constrained and information on the lithospheric mantle in cratonic regions is limited to studies of sulfide inclusions in diamonds. The $\delta^{34}\text{S}$ values of sulfide inclusions in peridotitic diamonds vary between -4 and +6‰ (Fig. 1), with a mode centred on the chondritic value. Sulfur isotope measurements of sulfide grains in SCLM peridotites exhibit a similar $\delta^{34}\text{S}$ range, between -6 and +7‰ (Fig. 1). Conversely, the $\text{S}_{\text{sulfide}}$ isotope systematics of bulk peridotite xenoliths from the SCLM is skewed towards positive values (Fig. 1). Based on this observation, Ionov et al. (1992) suggested that a $\delta^{34}\text{S}$ value of +2‰ is representative of the SCLM. ~~However, these bulk-rock measurements are at odds with ~200 new *in situ* determinations of sulfide grains from SCLM xenoliths and orogenic peridotites (France), which exhibit negative $\delta^{34}\text{S}$ values between -7.0 and -0.5‰ (Alard, 2015).~~

To provide additional constraints on the S isotope composition of the SCLM and explore the use of S isotope geochemistry to trace the source(s) of metasomatic mantle fluids/melts, we measured the S isotope systematics of five metasomatised mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa; Fig. 2). The S isotope investigation was complemented by detailed petrographic and mineral chemistry studies of the sulfide minerals. These data permit comparisons between *in*

situ sulfide and bulk-rock S isotope analyses of mantle peridotites. The results demonstrate that the bulk S isotope determinations are not representative of mantle values, unless the host sulfide minerals are relatively fresh. Our study shows a limited range of S isotope compositions, which is remarkable given that the xenolith samples display different styles of metasomatic enrichment, which operated at distinct times. The S isotope systematics of these xenoliths is employed to provide new constraints on the source of metasomatic melts/[fluids](#) beneath the diamondiferous Kimberley region.

2. Geological setting

The mantle xenolith samples examined in this study originate from the Bultfontein Dumps, which hosts waste material from mining of the Bultfontein kimberlite. The Bultfontein kimberlite is part of the Kimberley cluster of kimberlites, which also includes the De Beers, Dutoitspan, Wesselson and Kimberley kimberlites, along with a number of smaller pipes, and is located in the SW part of the Kaapvaal craton (Fig. 2). Different dating techniques (i.e. U/Pb perovskite, Rb/Sr phlogopite, $^{40}\text{Ar}/^{39}\text{Ar}$ phlogopite) have produced variable emplacement age constraints, ranging between 81 and 90 Ma (Allsopp and Barrett, 1975; Fitch and Miller, 1983; Griffin et al., 2014). The Kimberley kimberlites are well known for hosting a variety of mantle xenoliths showing distinct metasomatic styles, e.g., MARID (mica-amphibole-rutile-ilmenite-diopside), PIC (phlogopite-ilmenite-clinopyroxene), glimmerites, polymict breccias, websterites, wehrlites, etc.

3. Samples and methods

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153 For this study we selected five phlogopite-bearing mantle xenolith samples exhibiting
154 different styles of metasomatic enrichment (Table 1; Supplementary Material, Fig.
155 S1). This collection includes a mantle polymict breccia (DU-1; Giuliani et al., 2013a,
156 2014b), a clinopyroxene-bearing spinel harzburgite (XM1/142), a LIMA (Lindsleyite-
157 MATHIASITE group of titanates) bearing spinel lherzolite (XM1/341; Giuliani et al.,
158 2014c), a LIMA, ilmenite and clinopyroxene-bearing spinel harzburgite (XM1/345;
159 Giuliani et al., 2014c) and a wehrlite (XM1/371). The polymict breccia consists of
160 abundant porphyroclasts of olivine, garnet, pyroxene and phlogopite, set in a matrix
161 of olivine, orthopyroxene, phlogopite, ilmenite, rutile and minor sulfides. The matrix
162 phases in polymict breccias are considered to have crystallized from an early pulse of
163 kimberlite magma at mantle depths (Giuliani et al., 2014b; Lawless et al., 1979;
164 Zhang et al., 2000). Samples XM1/341 and XM1/345 show a broadly similar
165 metasomatic overprint (e.g., occurrence of LIMA, similar compositions of phlogopite
166 and olivine), which differs from the type and composition of minerals in the other
167 xenoliths (Table 1). Samples XM1/142, XM1/341, XM1/345 and DU-1 derive from a
168 relatively limited depth range between ~100-125 km (i.e. ~3.0-3.8 GPa), whereas
169 xenolith XM1/371 was entrained from deeper in the mantle (~5.1 GPa, corresponding
170 to ~170 km; Table 1).

171 The polymict breccias from the Kimberley kimberlites probably formed in the
172 lithospheric mantle at between 80-90 Ma, i.e. coeval with kimberlite magmatism in
173 the area (Giuliani et al., 2014b; Lawless et al., 1979). U/Pb dating of two zircon grains
174 from a different off-cut of sample XM1/142 returned concordant ages of 82 ± 3 and
175 83 ± 2 Ma (1 σ ; Konzett et al., 2000); whereas the U/Pb ages of LIMA grains from
176 samples XM1/341 and XM1/345 are 177 ± 12 and 178 ± 29 Ma (2 σ ; [Giuliani et al.](#),

2014c). No age constraints are available for the metasomatism of xenolith XM1/371.

In summary, these samples experienced different styles of metasomatic enrichment at different times and slightly different depths.

Petrographic examination of multiple (≥ 3) thin sections from each sample shows that sulfides are common in all samples except XM1/371, where only one small ($< 10 \mu\text{m}$) Cu-rich sulfide grain was observed included in clinopyroxene. This sulfide-poor sample was selected to monitor possible effects of contamination by the kimberlite magma or crustal fluids.

Sulfide grains in polished thin sections and epoxy mounts were examined using a petrographic microscope and a scanning electron microscope (SEM). Their major-element compositions were quantified using a Cameca SX-50 electron microprobe (EMP) at the University of Melbourne. The S isotope composition of pentlandite and chalcopyrite grains was measured *in situ* by secondary-ion mass spectrometry (SIMS) using the Cameca 1280 Ion Probe housed at the Centre for Microscopy and Microanalysis (CMCA) of the University of Western Australia. Small, fresh off-cuts of samples XM1/142, XM1/341, XM1/345 and XM1/371 were selected for bulk-rock determination of S isotope compositions at the University of Maryland employing a ThermoFisher MAT 253 isotope ratio mass spectrometer. Sample DU-1 was not included in this latter study as it is characterised by extreme mineralogical and compositional heterogeneity, as is typical of polymict breccias (e.g., Giuliani et al., 2013a, 2014b; Zhang et al., 2000). Thus, different parts of this xenolith could have distinct S isotope compositions and the aim of our study is to compare *in situ* and bulk sample S isotope values representative of the same domain. Details of the analytical methods are provided in Supplementary Material.

4. Sulfide petrography

Sulfide grains in the studied samples are heterogeneously distributed and show variable degrees of alteration. In samples XM1/142, XM1/341 and XM1/345 pentlandite ((Fe,Ni)₉S₈) is the only sulfide phase of mantle origin and is partially replaced by mixtures of magnetite and heazlewoodite (Ni₃S₂). Small (≤10 μm) heazlewoodite grains are dispersed in the serpentine veins that pervasively traverse these xenoliths.

In sample XM1/142 pentlandite is closely associated with other metasomatic phases, i.e. clinopyroxene and phlogopite (Fig. 3a), and also occurs included in orthopyroxene. Pentlandite grains are up to 400-450 μm across and show a complex structure that includes ‘blades’ and ‘rods’ with a Ni-rich composition, Fe-rich highly fractured domains and minor (<10 vol.%) small (up to 20-25 μm) segregations of magnetite (Fig. 3b,c). The majority of observed grains (≥90%) are fresh with only minor alteration to heazlewoodite ± magnetite, even though all pentlandite grains are cut by networks of serpentine veinlets. The magnetite segregations are always connected to these serpentine veinlets.

Pentlandite also occurs in close association with clinopyroxene, ~~and~~ phlogopite and orthopyroxene in sample XM1/341. Compared to sample XM1/142, these pentlandite grains are ~~only~~ fresh (i.e. minor replacement by heazlewoodite + magnetite) only where included in clinopyroxene (Fig. 3d) and, occasionally, phlogopite. The inclusions are relatively widespread (~4-5 per thin section) and their size ranges between 20-60 μm. Interstitial grains (up to 300 μm in length) are less common (~2-3 per thin section) and extensively altered to micro-porous magnetite with abundant μm-sized inclusions of heazlewoodite and smaller domains of

homogeneous, inclusion-free heazlewoodite (Fig. 3e,f). We infer that magnetite and heazlewoodite replace former pentlandite, because pentlandite is the only fresh sulfide that was detected in the metasomatic phases clinopyroxene and phlogopite. Two small (~30 µm) inclusions of Fe-rich sulfide (monosulfide solid solution (mss) or pyrrhotite) ± pentlandite were identified in orthopyroxene and olivine, respectively.

Sulfide grains in sample XM1/345 are largely altered. Sulfides form large (up to ~1 mm), interstitial segregations, which are concentrated in specific parts of the sample corresponding to zones of phlogopite (± ilmenite ± LIMA) enrichment. Fresh pentlandite remnants are locally preserved in these segregations, which are otherwise altered to micro-porous magnetite and lesser heazlewoodite (Fig. 3g). Abundant sulfide inclusions occur in partially serpentinised orthopyroxene, but have been largely replaced by heazlewoodite and magnetite. Only a few small (<20 µm) unfractured inclusions are preserved and consist of pentlandite ± mss/pyrite/pyrrhotite.

Nickel-Cu-Fe sulfides are part of the magmatic matrix in polymict breccia sample DU-1, which cements the silicate porphyroclasts, and also forms large (up to 2.0×0.5 cm) segregations (Fig. 3h; see also Giuliani et al., 2013a). The fresh parts of these sulfide segregations are composed of intergrown pentlandite and chalcopyrite (Fig. 3i) and rare pyrrhotite with minor secondary Cu and Ni sulfides (i.e. digenite, chalcocite and heazlewoodite). Large parts of the sulfide segregations have been replaced by micro-porous magnetite (± hematite) with lesser Cu and Ni sulfides and native Cu.

In summary, pentlandite is the dominant sulfide phase in samples XM1/142, XM1/341 and XM1/345, and is closely associated with clinopyroxene and/or phlogopite. The sulfide grains are progressively more altered in the sequence XM1/142 (mainly fresh), XM1/341 (most inclusions are fresh), XM1/345 (only

remnant pentlandite). Conversely, sample DU-1 hosts mixtures of altered Ni-Fe and Cu-Fe sulfides. Finally, sample XM1/371 is sulfide poor, with only a single Cu-rich sulfide inclusion observed in a clinopyroxene grain and rare grains of heazlewoodite associated with serpentine veins.

5. Sulfide major element compositions

Major element compositions of pentlandite, [heazlewoodite and, for sample DU-1, chalcopyrite](#) grains are presented in Supplementary Material, Table S1. For sample XM1/142 the presence of two texturally and compositionally distinct types of pentlandite in each sulfide grain is confirmed by EMP analyses. The two populations (i.e. Fe-rich fractured domains and Ni-rich ‘blades/rods’) are distinguished by different Ni/Fe (atomic) ratios (0.74-0.92 vs 1.16-1.42), but exhibit similar S, Co and Cu concentrations (Fig. 4).

For sample XM1/341 we could only obtain representative analyses for two grains, which show distinct compositions (Table S1 and Fig. 4). However, the anomalously high O content (~5 wt.%) coupled with lower Ni/Fe ratio and S, Co and Cu concentrations for one of these analyses indicates electron beam overlapping adjacent magnetite. Hence, it remains unclear if the XM1/341 pentlandite grains have variable composition.

Multiple analyses of fresh pentlandite remnants in the altered sulfide segregations of sample XM1/345 yielded the highest Ni (40.1 ± 1.4 wt.%, 1sd) and Co (1.4 ± 0.3 wt.%) values of all xenoliths (Table S1 and Fig. 4). An EMP traverse across one pentlandite grain from this sample shows no intra-grain variations in fresh

pentlandite with compositional changes due to inclusions of heazlewoodite and/or serpentine within the analytical spots (Supplementary Material, Fig. S2).

~~DU-1-p~~Pentlandite and chalcopyrite in sample DU-1 shows ~~similar atomic proportions of Ni and Fe~~ variable composition (e.g., variable Ni/Fe ratio and Cu contents in pentlandite; Fig. 4; see also Giuliani et al., 2013a).

6. Sulfur isotopes

6.1. *In situ* analyses of pentlandite and chalcopyrite

The results of *in situ* S isotope analyses are presented in Supplementary Material Table S2. The pentlandite data-set includes ~~54-50~~ analyses from four samples and the overall $\delta^{34}\text{S}$ range is between ~~-65.9~~ and -1.4‰ (Fig. 5a). A total of ~~25~~ 15 analyses of chalcopyrite from sample DU-1 show $\delta^{34}\text{S}$ variations between ~~-6.25.4~~ and -1.0‰ (Fig. 5b). Measured $\Delta^{33}\text{S}$ values for the analysed sulfides are all within uncertainty of the chondritic value.

The S isotopic compositions of three pentlandite grains from sample XM1/142 cover a $\delta^{34}\text{S}$ range between -5.3 and -2.1‰ (mean $-4.2 \pm 1.0\text{‰}$ (1sd, 15 analyses)). Two grains (142_1_21 and 142_1_11), for which nine and four *in situ* analyses were obtained, shows intra-grain variations (-5.3 to -4.1 and -4.8 to -2.1‰ , respectively) exceeding the 2σ analytical uncertainty ($\sim 0.4\text{‰}$; Supplementary Material, Fig. S3).

Only one representative S isotope analysis of a pentlandite inclusion in clinopyroxene was obtained for sample XM1/341. The $\delta^{34}\text{S}$ value of this grain is ~~-5.9~~ $4 \pm 0.41.2\text{‰}$ (2σ).

For sample XM1/345 we measured the S isotope composition of four interstitial segregations. The analyses show within sample ($\delta^{34}\text{S} = -65.9$ to -2.6‰ ; mean $-54.4 \pm 1.42\text{‰}$ (1sd, 11 analyses)) and across grain variations (up to 20.9‰ ; Fig. 5c). It is noteworthy that analyses of pentlandite and heazlewoodite mixtures (not reported in Table S2) returned heavier S isotopic compositions than pure pentlandite from the same segregation (e.g., Fig. 5c). However, because the instrumental isotopic fractionation factor for heazlewoodite is unknown, we cannot confirm that heazlewoodite has higher $\delta^{34}\text{S}$ values than coexisting pentlandite.

Pentlandite and chalcopyrite in polymict breccia sample DU-1 show indistinguishable S isotopic compositions ($\delta^{34}\text{S} = -65.4.9$ to -1.4‰ ; mean $-312.9 \pm 1.10.9\text{‰}$ (1sd, 27 analyses); and $\delta^{34}\text{S} = -6.25.4$ to -1.0‰ ; mean $-312.6 \pm 1.54\text{‰}$ (1sd, 25 analyses), respectively), which cover most of the range observed in this study.

6.2. Bulk-rock values

Bulk-sample $\delta^{34}\text{S}$ values vary between -3.41‰ (XM1/142) and $+0.77\text{‰}$ (XM1/345; Supplementary Material Table S2). It is noteworthy that the mean value of the *in situ* S isotope analyses only overlaps the bulk-rock value in sample XM1/142 (Fig. 6), which is the only sample with predominantly fresh sulfides. The bulk-rock $\delta^{34}\text{S}$ values increase in the sequence XM1/142 to XM1/341 to XM1/345. The bulk $\delta^{34}\text{S}$ value of sulfide-poor xenolith sample XM1/371 is -0.66‰ . Only one of the four measured samples shows a large enough $\Delta^{33}\text{S}$ ($\Delta^{33}\text{S} = 0.079 \pm 0.016\text{‰}$ XM1/341) to suggest a mass independent fractionation (MIF), with the other samples being similar to, or

within uncertainty, of the chondritic value (Fig. 6 and Supplementary Material, Table S2).

7. Discussion

Sulfide minerals in the Bultfontein xenoliths are closely associated with metasomatic minerals, such as clinopyroxene, phlogopite, ilmenite and LIMA (e.g., Fig. 3a). Samples XM1/341 and XM1/345 experienced metasomatism by Ti-rich silicate melts and, hence, sulfide addition at ~177 and 178 Ma, respectively, i.e. coeval with the Karoo magmatic event (Giuliani et al., 2014c). Conversely, sulfide minerals crystallised in sample XM1/142 at ~82-83 Ma from a MARID-related melt/fluid (Konzett et al., 2000). In mantle polymict breccia DU-1 sulfides were produced by a kimberlitic melt just prior to kimberlite magma emplacement in the crust at ~80-90 Ma (Lawless et al., 1979; Giuliani et al., 2014b). Therefore, this study records the S isotope signature of metasomatic events affecting the same mantle domain (~100-125 km beneath Kimberley), but at distinct times (Table 1).

The S isotope compositions of sulfide minerals can be utilised to provide constraints on the source of metasomatic melts/fluids, inasmuch as the sulfide isotopic signatures reflects parental ~~melt~~-fluid compositions. This inference assumes negligible modification of the parental ~~melt~~-fluid composition by processes such as wall rock assimilation and isotopic exchange. Because there is negligible S isotopic fractionation between molten and solid sulfides (or between silicate melts and crystalline sulfides) at high temperature (Marini et al., 2011; Ohmoto and Rye, 1979), the S isotopic composition of sulfides will closely reflect the parental melt signature. However, significant isotopic fractionation (up to ~4-5‰ $\delta^{34}\text{S}$) between oxidised (i.e.

sulfate) and reduced S (i.e. sulfide) can occur even at $T \geq 900^\circ\text{C}$ (Ohmoto and Rye, 1979). While sulfate metasomatism has been recently reported in the lithospheric mantle beneath Kimberley (Giuliani et al., 2013b), the coexistence of sulfate and sulfide species in a melt/fluid or as solid phases requires unusual oxidising conditions, which are unlikely long-lived features of the lithospheric mantle. Likewise, at the reducing conditions of the lithospheric mantle, the major S species in C-O-H fluids is H_2S (plus other reduced compounds) and there is negligible S isotope fractionation between H_2S and Ni-Cu-Fe sulfides at the temperature recorded by the sulfide-rich xenolith samples ($750\text{-}900^\circ\text{C}$; Table 1) or higher (Li and Liu, 2006; Ohmoto and Rye, 1979).

The above discussion shows that the S isotope composition of mantle sulfides is representative of their parental melts/fluids. However, sulfide minerals that crystallise at high temperature are not stable at lower temperatures and re-equilibrate to polymineralic sulfide assemblages (e.g., Craig and Kullerud, 1969; Lorand and Luguet, 2016 and references therein). In the next section, we will address the effect of low-T sulfide re-equilibration on the S isotopic signature of mantle sulfides.

7.1. Low-temperature sulfide re-equilibration

Figure 4e shows that pentlandite is not stable at mantle conditions ($T \sim 800\text{-}900^\circ\text{C}$) where the Bultfontein mantle xenoliths were entrained by the kimberlite magma (see Table 1). Pentlandite along with variable amounts of pyrrhotite can derive from low-temperature re-equilibration between monosulfide solid solution (mss) and coexisting $(\text{Ni,Fe})_{3\pm x}\text{S}_2$ (i.e. high-T heazlewoodite solid solution) (Kullerud, 1963). Pyrrhotite and pentlandite can also exsolve from high-T mss in presence of fluids at upper

crustal conditions (Lorand and Luguet, 2016 and references therein). These processes can only occur at $T < 610^{\circ}\text{C}$, which demarks the upper stability limit of pentlandite (Kullerud, 1963). Pentlandite and Fe-rich sulfide (mss or pyrrhotite) only coexist in few unfractured inclusions in silicate minerals of samples XM1/341 and XM1/345. Conversely, pentlandite in fractured inclusions and interstitial sulfide assemblages in samples XM1/142 (Fig. 3a), XM1/341 (Fig. 3d) and XM1/345 (Figs. 3g and 5c) is closely associated with heazlewoodite, magnetite and serpentine. The pentlandite $\pm$ heazlewoodite $\pm$ magnetite assemblages documented in these samples XM1/142 (Fig. 3e) and XM1/341 (inclusions in silicate minerals; Fig. 3d), and previously studied mantle xenoliths from the Kaapvaal craton (Lorand and Gregoire, 2006), could originate from partial desulfidation of high-T monosulfide solid solutions (mss) during serpentinisation (Lorand and Gregoire, 2006). However, in sample XM1/142 the freshest sulfides consist of pentlandite with only minor magnetite and serpentine and without heazlewoodite (Fig. 3c). We interpret these assemblages to be former pentlandite $\pm$ pyrrhotite (or mss) intergrowths with magnetite replacing pyrrhotite during post-emplacement serpentinisation. However, aggregates of pentlandite and pyrite after mss are common in magmatic ore deposits (e.g., Craig and Kullerud, 1969) and also occur in metasomatised mantle xenoliths (e.g., Lorand, 1989). Therefore, it is possible that mss broke down to pentlandite + pyrite and magnetite replaced pyrite during post-emplacement serpentinisation. This is consistent with the observation that the magnetite patches in XM1/142 sulfides are always connected to the networks of serpentine veins traversing the sulfide grains (Fig. 3c).

Desulfidation of mss to pentlandite-rich aggregates and re-equilibration of mss $\pm (\text{Ni,Fe})_{3+x}\text{S}_2$ to pentlandite + pyrrhotite can fractionate the S isotope systematics of pentlandite from that of precursor high-T mantle sulfides. We have modelled the T_0

constrain to extent of S isotope variation S isotope variations associated with pentlandite formation from high-T mss assuming equilibrium conditions and employing the S isotope fractionation factors of Ohmoto and Rye (1979) and Li and Liu (2006) (see 'Modelling of S isotope fractionation' in Supplementary Material). At the likely conditions of mss desulfidation (i.e. $T \geq 200^\circ\text{C}$; Lorand and Gregoire, 2006), there is negligible S isotope fractionation between pentlandite and precursor mss (up to 0.5‰ $\delta^{34}\text{S}$ assuming 40 wt.% of S is removed from the sulfide assemblage as H_2S in a fluid phase). For pentlandite + pyrrhotite formation after mss $\pm (\text{Ni,Fe})_{3+x}\text{S}_2$, the S isotope fractionation between pentlandite and high-T mantle sulfides is equally limited (i.e. up to 0.7‰ $\delta^{34}\text{S}$ for pentlandite/pyrrhotite relative proportions of 50/50% and T of 300°C ; during retrogression of mss to pentlandite + pyrite, we carried out mass balance calculations assuming pentlandite/pyrite relative proportions between 90/10% (which approximates sample XM1/142) and 70/30% (more general case). We have assumed S isotope fractionation under equilibrium conditions and employed the pyrite- H_2S fractionation factor of Ohmoto and Rye (1979) and, in absence of a pentlandite fractionation factor, the violarite (FeNi_2S_3)- H_2S factor of Li and Liu (2006) (violarite being the only Ni-Fe sulfide for which a fractionation factor is available). The violarite (pentlandite)-pyrite S isotope fractionation factor is given by:

$$\delta^{34}\text{S}_{\text{violarite-pyrite}} = \delta^{34}\text{S}_{\text{violarite-H}_2\text{S}} - \delta^{34}\text{S}_{\text{pyrite-H}_2\text{S}} \quad (1)$$

The equilibration T between pentlandite and pyrite probably exceeds 200°C (Lorand, 1989); hence this temperature can be utilised to provide a maximum value for S isotopic fractionation. For pentlandite/pyrite relative proportions of 90/10%, pentlandite $\delta^{34}\text{S}$ is only 0.3‰ lower than the precursor mss. This value increases to 0.9‰ for a 70/30% ratio (Supplementary Material, Fig. S54), i.e. there is only a marginal difference between the isotopic compositions of pentlandite and the

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~~precursor mss.~~ Therefore, the S isotopic composition of pentlandite grains can be considered similar to precursor high-T mantle sulfides and, hence, representative of the parental melt composition.

7.2. Post-emplacement modification of bulk-rock S isotope compositions

In this section we consider possible reasons to account for the significant difference between bulk-rock and sulfide S isotope compositions from the same sample. Among the three samples investigated using *in situ* and bulk-rock S sulfide isotope measurements, only xenolith XM1/142 shows overlapping average *in situ* and bulk $\delta^{34}\text{S}$ values (-4.2 ± 1.0 and -3.4% , respectively; Fig. 6 and Table S2). This is noteworthy given that XM1/142 is the only sample where the majority of sulfides ($\geq 90\%$) are predominantly fresh (Fig. 3a,b). This result also represents validation of the SIMS analytical protocol adopted for the *in situ* analyses of pentlandite. For samples XM1/341 and XM1/345, the bulk-rock $\delta^{34}\text{S}$ results are higher than the mean values of the *in situ* sulfide analyses (Fig. 6).

The bulk S isotopic composition of mantle xenoliths in kimberlites can be affected by interaction with the transporting kimberlite magma or crustal fluids that commonly circulate in kimberlite pipes after magma emplacement (e.g., Afanasyev et al., 2014; Giuliani et al., 2014a and references therein). Country rocks in the Kimberley area, particularly shales, host abundant sulfide minerals (Giuliani, unpublished); hence contact metamorphism during kimberlite emplacement might release S-rich solutions into the kimberlite pipe that could contaminate mantle S signatures. The S isotopic compositions of shales from the Kimberley area are dominated by negative $\delta^{34}\text{S}$ values between -37 and 0% , with a single analysis at

+2‰ (Tsai et al., 1979). Interaction with fluids released from these shales would probably introduce very negative $\delta^{34}\text{S}$ values, which contrasts with the elevated bulk $\delta^{34}\text{S}$ values of xenoliths XM1/341 and XM1/345 (Fig. 6).

Magmatic sulfides in kimberlite rocks show a restricted S isotopic range of between -0.1‰ and +2.5‰ $\delta^{34}\text{S}$ (Giuliani et al., 2014a; Fig. 1). It is noteworthy that the bulk $\delta^{34}\text{S}$ value of xenolith XM1/371, which is sulfide poor, is $-0.66 \pm 0.30\text{‰}$; i.e. within uncertainty of the S isotopic composition ($-0.1 \pm 1.0\text{‰}$) of pyrrhotite from the Bultfontein kimberlite (Chaussidon et al., 1989). Therefore, the S isotope signature of sample XM1/371 might be dominated by kimberlite-related sulfides (e.g., heazlewoodite grains dispersed in serpentine veins). It is possible that interaction with kimberlite melts/fluids could have increased the bulk $\delta^{34}\text{S}$ values of samples

XM1/341 and XM1/345 (see Fig. 6). ~~Mass balance calculations, using the *in situ* $\delta^{34}\text{S}$ values of XM1/341 and XM1/345 sulfides as starting ‘mantle’ compositions and 0.1‰ $\delta^{34}\text{S}$ for the kimberlite contaminant, fail to reproduce the bulk isotopic composition of sample XM1/345. This is because the kimberlite contaminant has a S isotopic composition intermediate between the *in situ* sulfide and bulk sample values. In the case of sample XM1/341, modelling indicates that ~72% of S could be of kimberlite derivation.~~ However, the XM1/341 (and XM1/345) sulfides are partly altered to low-S assemblages of magnetite and heazlewoodite, which suggests S removal rather than addition (see below). Therefore, while interaction with kimberlite magmas could modify the S isotopic composition of mantle xenoliths, the difference between *in situ* sulfide and bulk-sample $\delta^{34}\text{S}$ values requires a different explanation.

Sulfide minerals show increasing alteration, and hence S removal, in the sequence XM1/142 < XM1/341 < XM1/345. This trend is mirrored by the increasing difference between bulk-rock and average *in situ* $\delta^{34}\text{S}$ values ($0.8 \pm 0.4\text{‰}$ (1sd) for

474 XM1/142; $3.59 \pm 0.40.6\%$ for XM1/341; $5.81 \pm 1.42\%$ for XM1/345). In order to
 475 investigate the relationship between S loss and isotopic modification, we have
 476 estimated the amount of S loss for each sample using the following equation:
 477
$$\text{S loss (\%)} = 100 \times [\text{MEAN}(V_{\text{mss}}) - \text{MEAN}(V_{\text{Pn}} + \Psi \times V_{\text{Hz}})] / \text{MEAN}(V_{\text{mss}}) \quad (2)$$

 478 with $V_{\text{mss}} = V_{\text{Pn}} + V_{\text{Hz}} + V_{\text{Mgt}}$, (3)
 479 where V is the grain volume (approximated by its surface dimensions), mss , Pn , Hz
 480 and Mgt denote monosulfide solid solution (i.e. the precursor high-T mantle sulfide),
 481 pentlandite, heazlewoodite and magnetite, respectively, and Ψ is a factor (~ 0.8) that
 482 accounts for the lower S content of heazlewoodite compared to pentlandite. This
 483 equation assumes that the amount of S loss is approximated by the difference between
 484 the volume of the original mantle sulfide and that of residual pentlandite plus
 485 heazlewoodite. This calculation only provides first order estimates with large
 486 uncertainties (~~40~~ 20% or more expressed as 1σ), because it assumes that mss,
 487 pentlandite and heazlewoodite have same density and does not consider the amount of
 488 heazlewoodite dispersed in serpentine veins. The calculated S losses are ~ 13 , 60 and
 489 76% for samples XM1/142, XM1/341 and XM1/345, respectively.

490 Figure 7 shows the good correlation ($r^2 = 0.97999$) between calculated S loss
 491 and the difference between bulk-rock and average *in situ* $\delta^{34}\text{S}$ values for the three
 492 samples (even though we acknowledge that the statistical significance is debatable
 493 because the trend includes only 3 points). For the estimated S loss quantities, the
 494 isotopic composition of ~~the~~ lost S is similar for the three samples (i.e. $\delta^{34}\text{S}_{\text{lost S}} = -$
 495 9.2% for XM1/142, $-7.48.0\%$ for XM1/341 and -6.90% for XM1/345). The above
 496 evidence implies that S was partially removed from these samples by similar
 497 processes. In addition, the ~~strong~~ correlation between S loss and bulk $\delta^{34}\text{S}$ variation
 498 rules out the addition (and subsequent reduction) of sulfate species during interaction

with the kimberlite magma or hydrous fluids (which produced serpentinisation) as possible sources of isotopically heavy S.

The correlation between S loss and bulk $\delta^{34}\text{S}$ variation is supported somewhat by the inverse correlation between S concentrations and $\delta^{34}\text{S}$ values observed by Ionov et al. (1992) for a suite of mantle xenoliths from the Tariat basalts (Mongolia). Ionov et al. (1992) also documented that the coarse-grained fractions of some mantle xenoliths from central Asian alkali-basalts have lighter S isotope compositions than the corresponding bulk samples. This is similar to our results because for the coarse-grained fractions sulfides only occur as largely fresh inclusions in silicate minerals, whereas the bulk samples also include altered interstitial sulfides. Therefore, it appears likely that increased bulk $\delta^{34}\text{S}$ in mantle peridotites in response to sulfide alteration is a ubiquitous process.

Partial S loss during serpentinisation is a common feature of mantle peridotites (e.g., Lorand, 1990). Serpentinisation of peridotite rocks lying at or below the seafloor may produce large variations of bulk S and corresponding deviations from initially chondritic S isotopic compositions (e.g., Alt and Shanks, 2011; Alt et al., 2013; Delacour et al., 2008). The only documented process that decreases bulk S contents while increasing bulk $\delta^{34}\text{S}$ values in oceanic peridotites during serpentinisation is kinetic fractionation during partial oxidation of mantle sulfides (Alt and Shanks, 2011; Delacour et al., 2008). Under equilibrium conditions, partial oxidation of sulfides in serpentinised peridotites would decrease the $\delta^{34}\text{S}$ compositions of residual sulfides because the sulfate products would be enriched in heavy S. However, if this process is accompanied by kinetic fractionation, the sulfate products (and S-rich compounds produced during intermediate oxidation reactions) become enriched in the lighter S isotopes, as demonstrated experimentally by Fry et al. (1988) and Grinenko

and Mineyev (1992). Once the sulfate (and intermediate S-rich) compounds are removed from the system, the overall effect is decreased bulk S contents, coupled with increased bulk $\delta^{34}\text{S}$ values for of the serpentinised peridotites. In this regard, Chaussidon and Lorand (1990) noted that fresh sulfide inclusions and the residual parts of partly altered (serpentinised) interstitial sulfide grains, from the same peridotite samples, have identical S isotopic compositions. These authors concluded that serpentinisation does not alter the S isotopic composition of residual mantle sulfides. We suggest that heazlewoodite, which is produced during pentlandite alteration, carries the isotopically heavier S produced by partial oxidation of pentlandite under kinetic fractionation conditions. Heazlewoodite is the most abundant sulfide phase in samples XM1/341 and XM1/345; hence, its isotopic composition must dominate the bulk-rock signature of these xenoliths. Alternatively, alteration of pentlandite to heazlewoodite (plus magnetite) may be accompanied by isotopic fractionation under equilibrium conditions, with isotopically lighter S partitioned into the fluid phases and then removed from the system. However, no experimental or theoretical data are available to support this interpretation.

In summary, while sample XM1/142 (predominantly fresh sulfides) shows overlapping *in situ* sulfide and bulk-rock S isotope values (Fig. 6), the bulk isotopic compositions of samples XM1/341 and XM1/345 indicates modification during serpentinisation and sulfide alteration. Given that mantle peridotites are commonly affected by serpentinisation, it seems likely that both the S concentration (Lorand, 1990), and the S isotope systematics of bulk peridotite samples are often modified by alteration. This study and results presented by Ionov et al. (1992) indicate that sulfide alteration increases the bulk $\delta^{34}\text{S}$ value of peridotite rocks. It is therefore not surprising that the vast majority of bulk S isotope determinations for SCLM

peridotites give $\delta^{34}\text{S} > 0\text{‰}$ (Fig. 1). This contrasts with the negative *in situ* sulfide $\delta^{34}\text{S}$ values reported here ~~and by Alard (2015) for mantle xenoliths and orogenic peridotites from France~~. These results seem to contradict the conclusion of Ionov et al. (1992) that the SCLM has on average positive $\delta^{34}\text{S}$ composition.

7.3. Sulfur isotope signature of the lithospheric mantle beneath Kimberley

The *in situ* S isotope analyses of metasomatised mantle xenoliths from Bultfontein show intra-grain (up to 2.7‰ $\delta^{34}\text{S}$) and within-sample variations (up to 4.4‰) that exceed the SIMS 2 σ analytical uncertainty (~ 0.24 - 0.86‰ ; Table S2). Previous *in situ* determinations of sulfides in mantle peridotites documented even larger variations, up to 5.7 and 8.0‰ $\delta^{34}\text{S}$ across a single grain and rock sample, respectively (Chaussidon and Lorand, 1990; Chaussidon et al., 1989). Intra-grain variations in the current samples may be due to incomplete isotopic homogenisation during re-equilibration of high-T mss ($\pm (\text{Ni,Fe})_{3+x}\text{S}_2$) to pentlandite-rich assemblages possibly coupled with partial ablation of heazlewoodite ($\pm$ magnetite and/or serpentine) not exposed at surface (e.g., sample XM1/142). The wider compositional spectra of samples XM1/345 (43.3‰ $\delta^{34}\text{S}$) and DU-1 ($5.43.5$ and $5.2.4.4\text{‰}$ for pentlandite and chalcopyrite, respectively) require additional explanations.

The variable major-element compositions of silicate, oxide and sulfide minerals in polymict breccia sample DU-1 (Fig. 4; Giuliani et al., 2013a, 2014b) suggests that the isotopic variability of the DU-1 sulfides may be due to incomplete equilibration of the metasomatic assemblage. Likewise, Zhang et al. (2000) documented large O isotope disequilibrium in other polymict breccia samples from the Kimberley area. This conclusion is reinforced by the indistinguishable S isotope

systematics of DU-1 pentlandite and chalcopyrite (Fig. 5a,b), which derived from the same high-T Ni-Cu-rich sulfide melt (Giuliani et al., 2013a), but contrasts with the expected isotope fractionation between chalcopyrite and violarite (proxy for pentlandite) under equilibrium conditions ($\sim 1.4\%$ at $T = 200^\circ\text{C}$; Li and Liu, 2006).

For sample XM1/345, the isotopic variability in the sulfides is reflected by the variable trace element and Sr isotope systematics of LIMA and clinopyroxene (Giuliani, unpublished). Therefore, it seems likely that sample XM1/345 preserves evidence of interaction with multiple metasomatic melts of distinct isotopic composition. Similarly, Thomassot et al. (2009) and Evans et al. (2014) inferred S contributions from different sources to explain intra-sample S isotope variations for sulfide grains included in diamonds from the Jwaneng kimberlite (Botswana) and in high-pressure metamorphic rocks from the western Alps, respectively.

The current samples show a more restricted $\delta^{34}\text{S}$ range between ~~-65.9-9~~ and ~~-4.01.0‰~~, with no statistically meaningful differences between samples (Fig. 5a,b), compared to sulfides in previously studied mantle peridotites (~ -7 to $+6\%$; Fig. 1) ~~and sulfide inclusions in peridotitic diamonds (~ -4 to $+6\%$; Fig. 1)~~. The limited S isotopic variation of the Bultfontein xenolith sulfides is remarkable considering the distinct metasomatic styles and age of metasomatism for these samples (Table 1). The restricted S isotopic composition could indicate that i) the lithospheric mantle beneath Kimberley shows limited S isotope variations with $\delta^{34}\text{S}$ values between ~~~ -7.6~~ and -1% ; ii) the sulfides equilibrated with the entraining kimberlite magma and/or post-emplacment crustal fluids; or iii) the parental metasomatic melts periodically tapped a source with relatively homogeneous limited S isotope composition variability.

The first hypothesis is not consistent with the isotope systematics ($\delta^{34}\text{S} = -4$ to $+3\%$; Eldridge et al., 1991) of sulfide inclusions in peridotitic diamonds from the

Kimberley area (Koffiefontein, Jagersfontein, Finsch, Roberts Victor – Fig. 2). Magmatic sulfides in kimberlites investigated thus far have $\delta^{34}\text{S}$ values between -0.1 and +2.5‰ (Fig. 1; Giuliani et al., 2014a). Therefore, isotopic equilibration with kimberlite melts would produce circa-chondritic S isotope compositions, clearly distinct from the observed range. Interaction with hydrous fluids after kimberlite emplacement may have contributed to the scatter of S isotope values, but not their homogenisation. Indeed, the *in situ* analyses of sulfides displaying different degrees of alteration (i.e. XM1/142 vs XM1/345) and, therefore, interaction with hydrous fluids, produce similar results (average $\delta^{34}\text{S} = -4.2 \pm 1.0$ vs ~~-5.14.4~~ ± 1.42 ‰ (1sd), respectively). Our preferred interpretation is that metasomatic ~~melts-fluids~~ operating beneath Kimberley at ~180 and 90-80 Ma were sourced from a reservoir with limited S isotope variations.

Recent studies of mid-ocean ridge basalts (MORB) by Labidi et al. (2012, 2013, 2014) revealed that the asthenospheric mantle has a $\delta^{34}\text{S}$ signature < 0 ‰ and, more probably, ≤ -1.4 ‰. Therefore, the asthenospheric mantle is a possible source of S for the metasomatic melts. However, the isotopic composition of sulfides in the Bultfontein xenoliths extends to $\delta^{34}\text{S}$ values of ~~-65.9~~‰, which requires another S source(s). Sulfide grains in mantle eclogites and eclogitic diamonds show large $\delta^{34}\text{S}$ deviations from 0‰ (Fig. 1), which are attributed to the occurrence of recycled crustal S in the Earth's mantle (Eldridge et al., 1991; Thomassot et al., 2009). It is therefore likely that some S of crustal origin was present in the source of the metasomatic melts that affected the Bultfontein xenoliths.

The main contributor of S in subducted slabs is the oceanic crust with about 5/6 provided by the variably altered igneous section and 1/6 by the sedimentary cover (Alt et al., 2013). The altered upper (volcanic) section of the oceanic crust is

characterised by negative $\delta^{34}\text{S}$ values (e.g., Alt and Shanks, 2011) and, once subducted, could represent a possible S source for the metasomatic fluids. However, this hypothesis is not favoured because the S isotope profile across an entire section of oceanic crust reveals that the $\delta^{34}\text{S}$ signature of the altered igneous sector ($\sim 0.9\%$; Alt, 1995) is close to chondritic values. The sedimentary record shows large S isotopic variations for both seawater sulfates ($\delta^{34}\text{S} \geq 5\text{-}10\%$) and sedimentary pyrite through time (Fig. 1). Sedimentary pyrite exhibits predominantly positive $\delta^{34}\text{S}$ values until ~ 500 Ma and largely negative values thereafter (e.g., Farquhar et al., 2010). In this regard, Canfield (2004) proposed that a sulfur reservoir with negative $\delta^{34}\text{S}$ signature is missing in the Archean-Proterozoic sedimentary record and could have been subducted and stored in the Earth's mantle. It is important to note that studies of high-P and high-T metamorphic rocks have shown that S isotope compositions are not modified by prograde metamorphism (Cook and Hoefs, 1997; Evans et al., 2014 and references therein) and that S is partially retained and transferred into the mantle during high-P metamorphism of subducted rocks (Alt et al., 2013; Evans et al., 2014). We therefore propose that the metasomatic melts, which affected the Bultfontein xenoliths, originated from a source containing subducted sediments with negative $\delta^{34}\text{S}$ compositions. These sediments could represent the missing sedimentary reservoir implied by Canfield (2004). Subducted sediments, with distinct S isotopic compositions (i.e. $\delta^{34}\text{S} < \text{and} > 0\%$, respectively), are suggested to occur in the source(s) of ocean island basalts (OIB) from Mangaia (Polynesia; Cabral et al., 2013) and Samoa (Labidi et al., 2015).

Sulfide inclusions in olivine from the Mangaia lavas also show $\Delta^{33}\text{S} \neq 0$ ($\pm 0.42\%$), which indicates an Archean age for the recycled sediments (Cabral et al., 2013). Sulfur with significant MIF (i.e. $\Delta^{33}\text{S} \neq 0 \pm 0.42\%$) was also identified in

sulfide inclusions from eclogitic diamonds (Farquhar et al., 2002; Thomassot et al., 2009) and interpreted to reflect incorporation of Archean, surface-derived S in the mantle. Our *in situ* analyses of sulfides do not show any evidence of MIF, which may be partly due to the large analytical uncertainties associated with SIMS analyses (± 0.32 - 0.64‰ $\Delta^{33}\text{S}$; Table S2). In fact, the bulk analysis of sample XM1/341 reveals a $\Delta^{33}\text{S}$ value ($0.079 \pm 0.016\text{‰}$) that deviates ~~that deviates~~ slightly from the chondritic value. In contrast, the S isotopic compositions of other samples are similar to, or within uncertainty of 0‰ and plot in the $\Delta^{33}\text{S}$ range of MORBs (-0.00539 to $+0.011\text{‰}$; Labidi et al., 2012, 2013, 2014). Assuming that alteration of XM1/341 sulfides did not affect their $\Delta^{33}\text{S}$ values and the MORB range is representative of the asthenospheric mantle, the S isotopic composition of sample XM1/341 indicates that recycled crustal S was present in the source of the metasomatic melt that affected this xenolith. $\Delta^{33}\text{S}$ deviates significantly from 0‰ in sedimentary and volcanic rocks only before ~ 2.4 Ga (e.g., Farquhar and Wing, 2003); however, variations between -0.15 and $+0.134\text{‰}$ are documented after 2.4 Ga (Farquhar et al., 2010 and references therein). Therefore, the small MIF shown by sample XM1/341 does not provide any constraint on the age of the S-bearing recycled material.

8. Conclusions

This combined *in situ* sulfide and bulk-rock S isotope investigation of metasomatised mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa) provides new insights into the processes affecting the S isotope composition of mantle sulfides after their crystallisation in the mantle. Mass balance calculations show that re-equilibration of high-T ~~mss~~ mantle sulfides ($mss \pm (\text{Ni,Fe})_{3+x}\text{S}_2$) to low-T pentlandite-

~~rich assemblages ± pyrite~~ is accompanied by limited isotopic fractionation. Therefore, the isotope systematics of pentlandite are broadly representative of the parental metasomatic melt. Conversely, increasing rates of sulfide alteration and S removal during peridotite serpentinisation, fractionate the S isotopes between mantle sulfides and alteration products with an increase of the $^{34}\text{S}/^{32}\text{S}$ ratio in bulk peridotites. Bulk determinations of the S isotope composition of mantle peridotites are only representative of the mantle values if the sulfides are predominantly fresh. An important implication of this study is that previous bulk-rock determinations of mantle peridotite xenoliths, which are dominated by positive $\delta^{34}\text{S}$ values, require revision.

Sulfides in the Bultfontein xenoliths exhibit limited S isotope variations of between ~~-65.9~~ and -1.0‰ $\delta^{34}\text{S}$ despite of the variable style and age of metasomatic enrichment recorded by the samples. Our preferred interpretation is that metasomatic fluids operating beneath Kimberley at ~180 and 90-80 Ma were sourced from a reservoir with limited S isotope variations. This range is entirely consistent with new *in situ* determinations of sulfides in mantle xenoliths and orogenic peridotites from France (Alard, 2015), but differs from previous analyses of sulfide inclusions in peridotitic diamonds and sulfide grains in mantle peridotites (Fig. 1). Although our results are limited to the lithospheric mantle beneath Kimberley, we speculate that the SCLM may be dominated by negative $\delta^{34}\text{S}$ values once the results of Alard (2015) are included. The low $^{34}\text{S}/^{32}\text{S}$ composition of sulfides in the Bultfontein xenoliths suggest that the fluid source was probably located in the asthenospheric mantle and contained recycled crustal S ~~was present in the source of the metasomatic melts, which of sedimentary origin may be located in the asthenospheric mantle.~~

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883

Figure captions

Figure 1. Sulfur isotope ($\text{‰ } \delta^{34}\text{S}$ relative to VCDT) variations in marine sulfates (Farquhar et al., 2010 and references therein), sedimentary pyrite (Farquhar et al., 2010 and references therein), ocean island basalts (OIBs – Cabral et al., 2013; Chaussidon et al., 1989; Labidi et al., 2015), mid-ocean ridge basalts (MORBs – Labidi et al., 2012, 2013, 2014), bulk peridotite xenoliths entrained in the sub-continental lithospheric mantle (SCLM) by kimberlite and alkali-basalt magmas (Ionov et al., 1992; Kyser, 1990; Wilson et al., 1996), sulfides in SCLM peridotites (Chaussidon and Lorand, 1990; Chaussidon et al., 1989; Tsai et al., 1979) and in diamonds of peridotitic and eclogitic paragenesis (Eldridge et al., 1991; Cartigny et al., 2009; Chaussidon et al., 1987; Farquhar et al., 2002; Rudnick et al., 1993; Thomassot et al., 2009), sulfides in SCLM eclogite xenoliths sampled by kimberlite magmas (Chaussidon et al., 1989; Rudnick et al., 1993; Tsai et al., 1979; Vinogradov and Ilupin, 1972), and magmatic sulfides in kimberlites (Giuliani et al., 2014a and references therein).

Figure 2. Schematic map of southern Africa showing the location of the Kimberley cluster of kimberlites. The estimated boundary of the Kaapvaal craton and the location of major kimberlite and orangeite intrusions in the Kimberley area are also shown (RoVic = Roberts Victor).

Figure 3. Photomicrographs (a, c, h) and SEM-EDS images (b, d, e, f, g, i) of sulfide minerals in Bultfontein mantle xenoliths. a) XM1/142: pentlandite (Pn) grain associated with clinopyroxene (Cpx), spinel (Spl) and phlogopite (Phl). b, c)

XM1/142: micro-textures of pentlandite grains: (b) ‘Rods’ and ‘blades’ of Ni-rich pentlandite (Ni-Pn), and highly fractured domains of Fe-rich pentlandite (Fe-Pn); (c) minute (<10 µm) segregations of magnetite (Mgt) in a pentlandite grain traversed by abundant serpentine veins (not labelled). d) XM1/341: fractured inclusion of pentlandite (± magnetite) in clinopyroxene. e, f) XM1/341: aggregate of microporous magnetite and homogeneous, inclusion-free heazlewoodite after pentlandite; magnetite hosts abundant micron-sized inclusions of heazlewoodite. g) XM1/345: pentlandite remnant in interstitial aggregate of magnetite ± heazlewoodite. h, i) DU-1: sulfide segregation and (i) detail showing intergrown pentlandite and chalcopyrite (Cp), the latter being partly replaced by Cu sulfide (CuS). Ol: olivine; Ilm: ilmenite.

Figure 4. Co-variation plots of Ni/Fe atomic ratio vs (a) S (wt.%), (b) O (wt.%), (c) Co (atomic %) and (d) Cu (atomic %); and (e) atomic S – Fe – Ni+Co ternary plot for sulfide grains in Bultfontein mantle xenoliths. In panel (e), the ~900°C phase boundaries for high-temperature monosulfide solid solution (mss), Ni-rich sulfide liquid and 2-phase field from Craig and Kullerud (1969) are superimposed. Note that measured pentlandite compositions are not stable at these conditions.

Figure 5. *In situ* sulfur isotope (‰ $\delta^{34}\text{S}$ relative to VCDT) analyses of (a) pentlandite and (b) chalcopyrite grains in Bultfontein mantle xenoliths; (c) SEM-EDS image of sulfide grain in sample XM1/345 showing $\delta^{34}\text{S}$ variations (as ‰ units) measured by SIMS. Values reported in yellow represent mixtures of pentlandite and heazlewoodite and are not considered quantitative because the instrumental fractionation factor for heazlewoodite is unknown. Mgt: magnetite; Hz: heazlewoodite.

Figure 6. Comparison between the $\delta^{34}\text{S}$ (‰ relative to VCDT) and $\Delta^{33}\text{S}$ (‰) values of average *in situ* sulfide analyses and bulk-sample measurements. Error bars represent 1sd (standard deviation) for average *in situ* analyses and external reproducibility for bulk determinations. For sample DU-1 the *in situ* analyses of pentlandite (Pn) and chalcopyrite (Cp) are plotted using separate symbols. For sample XM1/341 only one *in situ* analysis was obtained. Dotted lines join *in situ* sulfide and bulk-rock determinations for the same xenolith sample. Note that the *in situ* sulfide and bulk-rock $\delta^{34}\text{S}$ values are only coincident for sample XM1/142.

Figure 7. Relationship between estimated S loss (wt.%) and the difference between $\delta^{34}\text{S}$ (‰ relative to VCDT) values of bulk-rock versus average *in situ* sulfide analyses for samples XM1/142, XM1/341 and XM1/345. Only one *in situ* analysis was obtained from sample XM1/341. A linear regression through the 3 points returns a R^2 value of 0.966999.

Sulfur isotope composition of metasomatised mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa): contribution from subducted sediments and the effect of sulfide alteration on S isotope systematics

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Highlights

- *In situ* sulfide and bulk-rock analysis of S isotopes for Kimberley mantle peridotites
- Limited isotope variability for *in situ* analyses ($\delta^{34}\text{S} \sim -6$ to -1‰)
- Bulk-rock $\delta^{34}\text{S}$ values overlap with average *in situ* results only if sulfides are fresh
- The S isotopic composition of the sub-continental lithospheric mantle requires revision
- Recycled ancient low- $^{34}\text{S}/^{32}\text{S}$ sediments in the mantle source of metasomatic fluids

1 **Sulfur isotope composition of metasomatised mantle xenoliths from**
2 **the Bultfontein kimberlite (Kimberley, South Africa): contribution**
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4 **isotope systematics**

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33 **Abstract**

34

35 Sulfur isotopes are a powerful geochemical tracer in high-temperature processes, but
36 have rarely been applied to the study of mantle metasomatism. In addition, there are
37 very limited S isotope data on sub-continental lithospheric mantle (SCLM) material.
38 For cratonic regions, these data are restricted to sulfide inclusions in diamonds. To
39 provide new constraints on the S isotope composition of the SCLM and on the
40 source(s) of mantle metasomatic fluids beneath the diamondiferous Kimberley region
41 (South Africa), we investigated the S isotope systematics of five metasomatised
42 mantle xenoliths from the Bultfontein kimberlite. Pentlandite and chalcopyrite in
43 these xenoliths were analysed by *in situ* secondary-ion mass spectrometry (SIMS),
44 with bulk-rock material measured by gas source isotope ratio mass spectrometry
45 techniques. Based on previous studies, the xenoliths experienced different types of
46 metasomatism to one another at distinct times (~180 and ~90-80 Ma). Contained
47 pentlandite grains show variable alteration to heazlewoodite (i.e. Ni sulfide) +
48 magnetite. The *in situ* S isotope analyses of pentlandite exhibit a relatively restricted
49 range between -5.9 and -1.4‰ $\delta^{34}\text{S}$ (compared to VCDT), with no statistically
50 meaningful differences between samples. Chalcopyrite only occurs in one sample and
51 shows $\delta^{34}\text{S}$ values between -5.4 and -1.0‰. The bulk-rock $\text{S}_{\text{sulfide}}$ isotope analyses

vary between -3.4 and +0.8‰ $\delta^{34}\text{S}$. Importantly, the only sample hosting dominantly fresh sulfides shows a bulk-rock $\delta^{34}\text{S}$ value consistent with the mean value for the sulfides, whereas the other samples exhibit higher bulk $^{34}\text{S}/^{32}\text{S}$ ratios. The differences between bulk-rock and average *in situ* $\delta^{34}\text{S}$ values are directly correlated with the degree of sulfide alteration. This evidence indicates that the elevated $^{34}\text{S}/^{32}\text{S}$ ratios in the bulk samples are not due to the introduction of heavy S (commonly as sulfates) and are best explained by isotopic fractionation coupled with the removal of light S during serpentinisation, when pentlandite is altered to S-poor mixtures of heazlewoodite and magnetite. Available bulk $\text{S}_{\text{sulfide}}$ isotopic data for SCLM peridotite xenoliths are dominated by positive $\delta^{34}\text{S}$ values, which contrasts with the negative values of the sulfides. These results imply that the mantle S isotope values from bulk peridotite samples are commonly modified by isotopic fractionation during serpentinisation. Therefore, the S isotopic composition of the SCLM may require revision. The limited isotopic variability shown by sulfides in the Bultfontein mantle xenoliths is probably due to intermittent tapping of a mantle source with a relatively restricted S isotope composition. While the asthenospheric mantle ($\delta^{34}\text{S} \leq -1.4\text{‰}$) is a viable candidate, $\delta^{34}\text{S}$ values as low as -5.9‰ require input from recycled crustal material, possibly represented by the sulfur reservoir with negative $\delta^{34}\text{S}$ signature that is missing in the >500 Ma sedimentary record and could have been subducted and stored in the Earth's mantle.

Keywords: sulfur isotopes; sulfides; mantle xenoliths; Kimberley; SIMS

1. Introduction

Sulfur isotopes provide an excellent geochemical tracer of high-temperature mantle processes, due to minimal isotope fractionation at high temperature (e.g., Ohmoto and Rye, 1979; Marini et al., 2011), unless redox reactions are involved, and large differences between mantle and crustal reservoirs (Fig. 1). Sulfur isotope ratios are not affected by partial melting or sulfide crystallisation from sulfide or silicate melts (Ohmoto and Rye, 1979; Marini et al., 2011). Sulfur isotope values for mantle-derived rocks, minerals and magmas that deviate significantly from $\delta^{34}\text{S}$ of 0‰ (compared to the Vienna Canon Diablo Troilite (VCDT) reference material) are commonly interpreted to reflect contributions of surface-derived S recycled into the Earth's mantle via subduction at convergent margins (e.g., Chaussidon et al., 1987; de Hoog et al., 2001; Eldridge et al., 1991; Ionov et al., 1992; Labidi et al., 2013, 2014, 2015; Thomassot et al., 2009; Wilson et al., 1996).

The discovery that extensive mass independent fractionation of S isotopes (expressed as ‰ $\Delta^{33}\text{S}$ variations compared to VCDT) only occurred until ~2.4 Ga (Farquhar and Wing, 2003 and references therein) has provided an additional tool to trace the incorporation of ancient recycled crustal S in the mantle. Studies of sulfide inclusions in diamonds (Farquhar et al., 2002; Thomassot et al., 2009) and olivine from ocean island basalts (Cabral et al., 2013) have demonstrated that mass-independent fractionated S can be preserved in the Earth's mantle.

Surprisingly, S isotope geochemistry has only been applied to genetic studies of metasomatic melts/fluids in the mantle on rare occasions (Chaussidon and Lorand, 1990; Ionov et al., 1992; Wilson et al., 1996). Ionov et al. (1992) and Wilson et al. (1996) attributed high $^{34}\text{S}/^{32}\text{S}$ ratios of bulk peridotite xenoliths from central Asia and Dish Hill (California), respectively, to metasomatism by slab-derived fluids. Chaussidon and Lorand (1990) suggested that high $\delta^{34}\text{S}$ values from sulfide grains in

orogenic peridotites from the Pyrenees (France) indicate the occurrence of recycled oceanic crust in the mantle source of the metasomatic melts. Conversely, metasomatism by asthenospheric fluids was advocated for Dish Hill mantle xenoliths with circa-chondritic bulk $\delta^{34}\text{S}$ values (Wilson et al., 1996).

The S isotope composition of the sub-continental lithospheric mantle (SCLM) is also poorly constrained and information on the lithospheric mantle in cratonic regions is limited to studies of sulfide inclusions in diamonds. The $\delta^{34}\text{S}$ values of sulfide inclusions in peridotitic diamonds vary between -4 and +6‰ (Fig. 1), with a mode centred on the chondritic value. Sulfur isotope measurements of sulfide grains in SCLM peridotites exhibit a similar $\delta^{34}\text{S}$ range, between -6 and +7‰ (Fig. 1). Conversely, the S_{sulfide} isotope systematics of bulk peridotite xenoliths from the SCLM is skewed towards positive values (Fig. 1). Based on this observation, Ionov et al. (1992) suggested that a $\delta^{34}\text{S}$ value of +2‰ is representative of the SCLM.

To provide additional constraints on the S isotope composition of the SCLM and explore the use of S isotope geochemistry to trace the source(s) of metasomatic mantle fluids/melts, we measured the S isotope systematics of five metasomatised mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa; Fig. 2). The S isotope investigation was complemented by detailed petrographic and mineral chemistry studies of the sulfide minerals. These data permit comparisons between *in situ* sulfide and bulk-rock S isotope analyses of mantle peridotites. The results demonstrate that the bulk S isotope determinations are not representative of mantle values, unless the host sulfide minerals are relatively fresh. Our study shows a limited range of S isotope compositions, which is remarkable given that the xenolith samples display different styles of metasomatic enrichment, which operated at distinct times. The S isotope systematics of these xenoliths is employed to provide new constraints

on the source of metasomatic melts/fluids beneath the diamondiferous Kimberley region.

2. Geological setting

The mantle xenolith samples examined in this study originate from the Bultfontein Dumps, which hosts waste material from mining of the Bultfontein kimberlite. The Bultfontein kimberlite is part of the Kimberley cluster of kimberlites, which also includes the De Beers, Dutoitspan, Wesselton and Kimberley kimberlites, along with a number of smaller pipes, and is located in the SW part of the Kaapvaal craton (Fig. 2). Different dating techniques (i.e. U/Pb perovskite, Rb/Sr phlogopite, $^{40}\text{Ar}/^{39}\text{Ar}$ phlogopite) have produced variable emplacement age constraints, ranging between 81 and 90 Ma (Allsopp and Barrett, 1975; Fitch and Miller, 1983; Griffin et al., 2014). The Kimberley kimberlites are well known for hosting a variety of mantle xenoliths showing distinct metasomatic styles, e.g., MARID (mica-amphibole-rutile-ilmenite-diopside), PIC (phlogopite-ilmenite-clinopyroxene), glimmerites, polymict breccias, websterites, wehrlites, etc.

3. Samples and methods

For this study we selected five phlogopite-bearing mantle xenolith samples exhibiting different styles of metasomatic enrichment (Table 1; Supplementary Material, Fig. S1). This collection includes a mantle polymict breccia (DU-1; Giuliani et al., 2013a, 2014b), a clinopyroxene-bearing spinel harzburgite (XM1/142), a LIMA (Lindsleyite-Mathiasite group of titanates) bearing spinel ilherzolite (XM1/341; Giuliani et al.,

2014c), a LIMA, ilmenite and clinopyroxene-bearing spinel harzburgite (XM1/345; Giuliani et al., 2014c) and a wehrlite (XM1/371). The polymict breccia consists of abundant porphyroclasts of olivine, garnet, pyroxene and phlogopite, set in a matrix of olivine, orthopyroxene, phlogopite, ilmenite, rutile and minor sulfides. The matrix phases in polymict breccias are considered to have crystallized from an early pulse of kimberlite magma at mantle depths (Giuliani et al., 2014b; Lawless et al., 1979; Zhang et al., 2000). Samples XM1/341 and XM1/345 show a broadly similar metasomatic overprint (e.g., occurrence of LIMA, similar compositions of phlogopite and olivine), which differs from the type and composition of minerals in the other xenoliths (Table 1). Samples XM1/142, XM1/341, XM1/345 and DU-1 derive from a relatively limited depth range between ~100-125 km (i.e. ~3.0-3.8 GPa), whereas xenolith XM1/371 was entrained from deeper in the mantle (~5.1 GPa, corresponding to ~170 km; Table 1).

The polymict breccias from the Kimberley kimberlites probably formed in the lithospheric mantle at between 80-90 Ma, i.e. coeval with kimberlite magmatism in the area (Giuliani et al., 2014b; Lawless et al., 1979). U/Pb dating of two zircon grains from a different off-cut of sample XM1/142 returned concordant ages of 82 ± 3 and 83 ± 2 Ma (1σ ; Konzett et al., 2000); whereas the U/Pb ages of LIMA grains from samples XM1/341 and XM1/345 are 177 ± 12 and 178 ± 29 Ma (2σ ; Giuliani et al., 2014c). No age constraints are available for the metasomatism of xenolith XM1/371. In summary, these samples experienced different styles of metasomatic enrichment at different times and slightly different depths.

Petrographic examination of multiple (≥ 3) thin sections from each sample shows that sulfides are common in all samples except XM1/371, where only one small ($< 10 \mu\text{m}$) Cu-rich sulfide grain was observed included in clinopyroxene. This

sulfide-poor sample was selected to monitor possible effects of contamination by the kimberlite magma or crustal fluids.

Sulfide grains in polished thin sections and epoxy mounts were examined using a petrographic microscope and a scanning electron microscope (SEM). Their major-element compositions were quantified using a Cameca SX-50 electron microprobe (EMP) at the University of Melbourne. The S isotope composition of pentlandite and chalcopyrite grains was measured *in situ* by secondary-ion mass spectrometry (SIMS) using the Cameca 1280 Ion Probe housed at the Centre for Microscopy and Microanalysis (CMCA) of the University of Western Australia. Small, fresh off-cuts of samples XM1/142, XM1/341, XM1/345 and XM1/371 were selected for bulk-rock determination of S isotope compositions at the University of Maryland employing a ThermoFisher MAT 253 isotope ratio mass spectrometer. Sample DU-1 was not included in this latter study as it is characterised by extreme mineralogical and compositional heterogeneity, as is typical of polymict breccias (e.g., Giuliani et al., 2013a, 2014b; Zhang et al., 2000). Thus, different parts of this xenolith could have distinct S isotope compositions and the aim of our study is to compare *in situ* and bulk sample S isotope values representative of the same domain. Details of the analytical methods are provided in Supplementary Material.

4. Sulfide petrography

Sulfide grains in the studied samples are heterogeneously distributed and show variable degrees of alteration. In samples XM1/142, XM1/341 and XM1/345 pentlandite ((Fe,Ni)₉S₈) is the only sulfide phase of mantle origin and is partially replaced by mixtures of magnetite and heazlewoodite (Ni₃S₂). Small ($\leq 10\ \mu\text{m}$)

heazlewoodite grains are dispersed in the serpentine veins that pervasively traverse these xenoliths.

In sample XM1/142 pentlandite is closely associated with other metasomatic phases, i.e. clinopyroxene and phlogopite (Fig. 3a), and also occurs included in orthopyroxene. Pentlandite grains are up to 450 μm across and show a complex structure that includes ‘blades’ and ‘rods’ with a Ni-rich composition, Fe-rich highly fractured domains and minor (<10 vol.%) small (up to 20-25 μm) segregations of magnetite (Fig. 3b,c). The majority of observed grains ($\geq 90\%$) are fresh with only minor alteration to heazlewoodite $\pm$ magnetite, even though all pentlandite grains are cut by networks of serpentine veinlets. The magnetite segregations are always connected to these serpentine veinlets.

Pentlandite also occurs in close association with clinopyroxene, phlogopite and orthopyroxene in sample XM1/341. Compared to sample XM1/142, these pentlandite grains are fresh (i.e. minor replacement by heazlewoodite + magnetite) only where included in clinopyroxene (Fig. 3d) and, occasionally, phlogopite. The inclusions are relatively widespread (~ 4 -5 per thin section) and their size ranges between 20-60 μm . Interstitial grains (up to 300 μm in length) are less common (~ 2 -3 per thin section) and extensively altered to micro-porous magnetite with abundant μm -sized inclusions of heazlewoodite and smaller domains of homogeneous, inclusion-free heazlewoodite (Fig. 3e,f). We infer that magnetite and heazlewoodite replace former pentlandite, because pentlandite is the only fresh sulfide that was detected in the metasomatic phases clinopyroxene and phlogopite. Two small (~ 30 μm) inclusions of Fe-rich sulfide (monosulfide solid solution (mss) or pyrrhotite) $\pm$ pentlandite were identified in orthopyroxene and olivine, respectively.

Sulfide grains in sample XM1/345 are largely altered. Sulfides form large (up to ~1 mm), interstitial segregations, which are concentrated in specific parts of the sample corresponding to zones of phlogopite ($\pm$ ilmenite $\pm$ LIMA) enrichment. Fresh pentlandite remnants are locally preserved in these segregations, which are otherwise altered to micro-porous magnetite and lesser heazlewoodite (Fig. 3g). Abundant sulfide inclusions occur in partially serpentinised orthopyroxene, but have been largely replaced by heazlewoodite and magnetite. Only a few small ($<20\ \mu\text{m}$) unfractured inclusions are preserved and consist of pentlandite $\pm$ mss/pyrrhotite.

Nickel-Cu-Fe sulfides are part of the magmatic matrix in polymict breccia sample DU-1, which cements the silicate porphyroclasts, and also forms large (up to $2.0\times 0.5\ \text{cm}$) segregations (Fig. 3h; see also Giuliani et al., 2013a). The fresh parts of these sulfide segregations are composed of intergrown pentlandite and chalcopyrite (Fig. 3i) and rare pyrrhotite with minor secondary Cu and Ni sulfides (i.e. digenite, chalcocite and heazlewoodite). Large parts of the sulfide segregations have been replaced by micro-porous magnetite ($\pm$ hematite) with lesser Cu and Ni sulfides and native Cu.

In summary, pentlandite is the dominant sulfide phase in samples XM1/142, XM1/341 and XM1/345, and is closely associated with clinopyroxene and/or phlogopite. The sulfide grains are progressively more altered in the sequence XM1/142 (mainly fresh), XM1/341 (most inclusions are fresh), XM1/345 (only remnant pentlandite). Conversely, sample DU-1 hosts mixtures of altered Ni-Fe and Cu-Fe sulfides. Finally, sample XM1/371 is sulfide poor, with only a single Cu-rich sulfide inclusion observed in a clinopyroxene grain and rare grains of heazlewoodite associated with serpentine veins.

5. Sulfide major element compositions

Major element compositions of pentlandite, heazlewoodite and, for sample DU-1, chalcopyrite grains are presented in Supplementary Material, Table S1. For sample XM1/142 the presence of two texturally and compositionally distinct types of pentlandite in each sulfide grain is confirmed by EMP analyses. The two populations (i.e. Fe-rich fractured domains and Ni-rich ‘blades/rods’) are distinguished by different Ni/Fe (atomic) ratios (0.74-0.92 *vs* 1.16-1.42), but exhibit similar S, Co and Cu concentrations (Fig. 4).

For sample XM1/341 we could only obtain representative analyses for two grains, which show distinct compositions (Table S1 and Fig. 4). However, the anomalously high O content (~5 wt.%) coupled with lower Ni/Fe ratio and S, Co and Cu concentrations for one of these analyses indicates electron beam overlapping adjacent magnetite. Hence, it remains unclear if the XM1/341 pentlandite grains have variable composition.

Multiple analyses of fresh pentlandite remnants in the altered sulfide segregations of sample XM1/345 yielded the highest Ni (40.1 ± 1.4 wt.%, 1sd) and Co (1.4 ± 0.3 wt.%) values of all xenoliths (Table S1 and Fig. 4). An EMP traverse across one pentlandite grain from this sample shows no intra-grain variations in fresh pentlandite with compositional changes due to inclusions of heazlewoodite and/or serpentine within the analytical spots (Supplementary Material, Fig. S2).

Pentlandite and chalcopyrite in sample DU-1 show variable composition (e.g., variable Ni/Fe ratio and Cu contents in pentlandite; Fig. 4; see also Giuliani et al., 2013a).

6. Sulfur isotopes

6.1. *In situ* analyses of pentlandite and chalcopyrite

The results of *in situ* S isotope analyses are presented in Supplementary Material Table S2. The pentlandite data-set includes 50 analyses from four samples and the overall $\delta^{34}\text{S}$ range is between -5.9 and -1.4‰ (Fig. 5a). A total of 15 analyses of chalcopyrite from sample DU-1 show $\delta^{34}\text{S}$ variations between -5.4 and -1.0‰ (Fig. 5b). Measured $\Delta^{33}\text{S}$ values for the analysed sulfides are all within uncertainty of the chondritic value.

The S isotopic compositions of three pentlandite grains from sample XM1/142 cover a $\delta^{34}\text{S}$ range between -5.3 and -2.1‰ (mean $-4.2 \pm 1.0\text{‰}$ (1sd, 15 analyses)). Two grains (142_1_21 and 142_1_11), for which nine and four *in situ* analyses were obtained, shows intra-grain variations (-5.3 to -4.1 and -4.8 to -2.1‰, respectively) exceeding the 2σ analytical uncertainty ($\sim 0.4\text{‰}$; Supplementary Material, Fig. S3).

Only one representative S isotope analysis of a pentlandite inclusion in clinopyroxene was obtained for sample XM1/341. The $\delta^{34}\text{S}$ value of this grain is $-5.4 \pm 1.2\text{‰}$ (2σ).

For sample XM1/345 we measured the S isotope composition of four interstitial segregations. The analyses show within sample ($\delta^{34}\text{S} = -5.9$ to -2.6‰ ; mean $-4.4 \pm 1.2\text{‰}$ (1sd, 9 analyses)) and across grain variations (up to 1.9‰ ; Fig. 5c). It is noteworthy that analyses of pentlandite and heazlewoodite mixtures (not reported in Table S2) returned heavier S isotopic compositions than pure pentlandite from the same segregation (e.g., Fig. 5c). However, because the instrumental isotopic

fractionation factor for heazlewoodite is unknown, we cannot confirm that heazlewoodite has higher $\delta^{34}\text{S}$ values than coexisting pentlandite.

Pentlandite and chalcopyrite in polymict breccia sample DU-1 show indistinguishable S isotopic compositions ($\delta^{34}\text{S} = -4.9$ to -1.4‰ ; mean $-2.9 \pm 0.9\text{‰}$ (1sd, 25 analyses); and $\delta^{34}\text{S} = -5.4$ to -1.0‰ ; mean $-2.6 \pm 1.4\text{‰}$ (1sd, 15 analyses), respectively), which cover most of the range observed in this study.

6.2. Bulk-rock values

Bulk-sample $\delta^{34}\text{S}$ values vary between -3.41‰ (XM1/142) and $+0.77\text{‰}$ (XM1/345; Supplementary Material Table S2). It is noteworthy that the mean value of the *in situ* S isotope analyses only overlaps the bulk-rock value in sample XM1/142 (Fig. 6), which is the only sample with predominantly fresh sulfides. The bulk-rock $\delta^{34}\text{S}$ values increase in the sequence XM1/142 to XM1/341 to XM1/345. The bulk $\delta^{34}\text{S}$ value of sulfide-poor xenolith sample XM1/371 is -0.66‰ . Only one of the four measured samples shows a large enough $\Delta^{33}\text{S}$ ($\Delta^{33}\text{S} = 0.079 \pm 0.016\text{‰}$ – XM1/341) to suggest a mass independent fractionation (MIF), with the other samples being similar to, or within uncertainty, of the chondritic value (Fig. 6 and Supplementary Material, Table S2).

7. Discussion

Sulfide minerals in the Bultfontein xenoliths are closely associated with metasomatic minerals, such as clinopyroxene, phlogopite, ilmenite and LIMA (e.g., Fig. 3a). Samples XM1/341 and XM1/345 experienced metasomatism by Ti-rich silicate melts

and, hence, sulfide addition at ~177 and 178 Ma, respectively, i.e. coeval with the Karoo magmatic event (Giuliani et al., 2014c). Conversely, sulfide minerals crystallised in sample XM1/142 at ~82-83 Ma from a MARID-related melt/fluid (Konzett et al., 2000). In mantle polymict breccia DU-1 sulfides were produced by a kimberlitic melt just prior to kimberlite magma emplacement in the crust at ~80-90 Ma (Lawless et al., 1979; Giuliani et al., 2014b). Therefore, this study records the S isotope signature of metasomatic events affecting the same mantle domain (~100-125 km beneath Kimberley), but at distinct times (Table 1).

The S isotope compositions of sulfide minerals can be utilised to provide constraints on the source of metasomatic melts/fluids, inasmuch as the sulfide isotopic signatures reflects parental fluid compositions. This inference assumes negligible modification of the parental fluid composition by processes such as wall rock assimilation and isotopic exchange. Because there is negligible S isotopic fractionation between molten and solid sulfides (or between silicate melts and crystalline sulfides) at high temperature (Marini et al., 2011; Ohmoto and Rye, 1979), the S isotopic composition of sulfides will closely reflect the parental melt signature. However, significant isotopic fractionation (up to ~4-5‰ $\delta^{34}\text{S}$) between oxidised (i.e. sulfate) and reduced S (i.e. sulfide) can occur even at $T \geq 900^\circ\text{C}$ (Ohmoto and Rye, 1979). While sulfate metasomatism has been recently reported in the lithospheric mantle beneath Kimberley (Giuliani et al., 2013b), the coexistence of sulfate and sulfide species in a melt/fluid or as solid phases requires unusual oxidising conditions, which are unlikely long-lived features of the lithospheric mantle. Likewise, at the reducing conditions of the lithospheric mantle, the major S species in C-O-H fluids is H_2S (plus other reduced compounds) and there is negligible S isotope fractionation between H_2S and Ni-Cu-Fe sulfides at the temperature recorded by the sulfide-rich

xenolith samples (750-900°C; Table 1) or higher (Li and Liu, 2006; Ohmoto and Rye, 1979).

The above discussion shows that the S isotope composition of mantle sulfides is representative of their parental melts/fluids. However, sulfide minerals that crystallise at high temperature are not stable at lower temperatures and re-equilibrate to polymineralic sulfide assemblages (e.g., Craig and Kullerud, 1969; Lorand and Luguet, 2016 and references therein). In the next section, we will address the effect of low-T sulfide re-equilibration on the S isotopic signature of mantle sulfides.

7.1. Low-temperature sulfide re-equilibration

Figure 4e shows that pentlandite is not stable at mantle conditions ($T \sim 800\text{-}900^\circ\text{C}$) where the Bultfontein mantle xenoliths were entrained by the kimberlite magma (see Table 1). Pentlandite along with variable amounts of pyrrhotite can derive from low-temperature re-equilibration between monosulfide solid solution (mss) and coexisting $(\text{Ni,Fe})_{3\pm x}\text{S}_2$ (i.e. high-T heazlewoodite solid solution) (Kullerud, 1963). Pyrrhotite and pentlandite can also exsolve from high-T mss in presence of fluids at upper crustal conditions (Lorand and Luguet, 2016 and references therein). These processes can only occur at $T < 610^\circ\text{C}$, which demarks the upper stability limit of pentlandite (Kullerud, 1963). Pentlandite and Fe-rich sulfide (mss or pyrrhotite) only coexist in few unfractured inclusions in silicate minerals of samples XM1/341 and XM1/345. Conversely, pentlandite in fractured inclusions and interstitial sulfide assemblages in samples XM1/142 (Fig. 3a), XM1/341 (Fig. 3d) and XM1/345 (Figs. 3g and 5c) is closely associated with heazlewoodite, magnetite and serpentine. The pentlandite $\pm$ heazlewoodite $\pm$ magnetite assemblages documented in these and previously studied

mantle xenoliths from the Kaapvaal craton (Lorand and Gregoire, 2006), could originate from partial desulfidation of high-T mss during serpentinisation (Lorand and Gregoire, 2006). However, in sample XM1/142 the freshest sulfides consist of pentlandite with only minor magnetite and serpentine and without heazlewoodite (Fig. 3c). We interpret these assemblages to be former pentlandite $\pm$ pyrrhotite (or mss) intergrowths with magnetite replacing pyrrhotite during post-emplacement serpentinisation.

Desulfidation of mss to pentlandite-rich aggregates and re-equilibration of mss $\pm$ (Ni,Fe)_{3 $\pm$ x}S₂ to pentlandite + pyrrhotite can fractionate the S isotope systematics of pentlandite from that of precursor high-T mantle sulfides. We have modelled the S isotope variations associated with pentlandite formation from high-T mss assuming equilibrium conditions and employing the S isotope fractionation factors of Ohmoto and Rye (1979) and Li and Liu (2006) (see ‘Modelling of S isotope fractionation’ in Supplementary Material). At the likely conditions of mss desulfidation (i.e. T $\geq$ 200°C; Lorand and Gregoire, 2006), there is negligible S isotope fractionation between pentlandite and precursor mss (up to 0.5‰ $\delta^{34}\text{S}$ assuming 40 wt.% of S is removed from the sulfide assemblage as H₂S in a fluid phase). For pentlandite + pyrrhotite formation after mss $\pm$ (Ni,Fe)_{3 $\pm$ x}S₂, the S isotope fractionation between pentlandite and high-T mantle sulfides is equally limited (i.e. up to 0.7‰ $\delta^{34}\text{S}$ for pentlandite/pyrrhotite relative proportions of 50/50% and T of 300°C; Supplementary Material, Fig. S5). Therefore, the S isotopic composition of pentlandite grains can be considered similar to precursor high-T mantle sulfides and, hence, representative of the parental melt composition.

7.2. Post-emplacement modification of bulk-rock S isotope compositions

400

401 In this section we consider possible reasons to account for the significant difference
402 between bulk-rock and sulfide S isotope compositions from the same sample. Among
403 the three samples investigated using *in situ* and bulk-rock S_{sulfide} isotope
404 measurements, only xenolith XM1/142 shows overlapping average *in situ* and bulk
405 $\delta^{34}\text{S}$ values (-4.2 ± 1.0 and -3.4% , respectively; Fig. 6 and Table S2). This is
406 noteworthy given that XM1/142 is the only sample where the majority of sulfides
407 ($\geq 90\%$) are predominantly fresh (Fig. 3a,b). This result also represents validation of
408 the SIMS analytical protocol adopted for the *in situ* analyses of pentlandite. For
409 samples XM1/341 and XM1/345, the bulk-rock $\delta^{34}\text{S}$ results are higher than the mean
410 values of the *in situ* sulfide analyses (Fig. 6).

411 The bulk S isotopic composition of mantle xenoliths in kimberlites can be
412 affected by interaction with the transporting kimberlite magma or crustal fluids that
413 commonly circulate in kimberlite pipes after magma emplacement (e.g., Afanasyev et
414 al., 2014; Giuliani et al., 2014a and references therein). Country rocks in the
415 Kimberley area, particularly shales, host abundant sulfide minerals (Giuliani,
416 unpublished); hence contact metamorphism during kimberlite emplacement might
417 release S-rich solutions into the kimberlite pipe that could contaminate mantle S
418 signatures. The S isotopic compositions of shales from the Kimberley area are
419 dominated by negative $\delta^{34}\text{S}$ values between -37 and 0% , with a single analysis at
420 $+2\%$ (Tsai et al., 1979). Interaction with fluids released from these shales would
421 probably introduce very negative $\delta^{34}\text{S}$ values, which contrasts with the elevated bulk
422 $\delta^{34}\text{S}$ values of xenoliths XM1/341 and XM1/345 (Fig. 6).

423 Magmatic sulfides in kimberlite rocks show a restricted S isotopic range of
424 between -0.1% and $+2.5\%$ $\delta^{34}\text{S}$ (Giuliani et al., 2014a; Fig. 1). It is noteworthy that

the bulk $\delta^{34}\text{S}$ value of xenolith XM1/371, which is sulfide poor, is $-0.66 \pm 0.30\text{‰}$; i.e. within uncertainty of the S isotopic composition ($-0.1 \pm 1.0\text{‰}$) of pyrrhotite from the Bultfontein kimberlite (Chaussidon et al., 1989). Therefore, the S isotope signature of sample XM1/371 might be dominated by kimberlite-related sulfides (e.g., heazlewoodite grains dispersed in serpentine veins). It is possible that interaction with kimberlite melts/fluids could have increased the bulk $\delta^{34}\text{S}$ values of samples XM1/341 and XM1/345 (see Fig. 6). However, the XM1/341 and XM1/345 sulfides are partly altered to low-S assemblages of magnetite and heazlewoodite, which suggests S removal rather than addition (see below). Therefore, while interaction with kimberlite magmas could modify the S isotopic composition of mantle xenoliths, the difference between *in situ* sulfide and bulk-sample $\delta^{34}\text{S}$ values requires a different explanation.

Sulfide minerals show increasing alteration, and hence S removal, in the sequence XM1/142 < XM1/341 < XM1/345. This trend is mirrored by the increasing difference between bulk-rock and average *in situ* $\delta^{34}\text{S}$ values ($0.8 \pm 0.4\text{‰}$ (1sd) for XM1/142; $3.9 \pm 0.6\text{‰}$ for XM1/341; $5.1 \pm 1.2\text{‰}$ for XM1/345). In order to investigate the relationship between S loss and isotopic modification, we have estimated the amount of S loss for each sample using the following equation:

$$\text{S loss (\%)} = 100 \times [\text{MEAN}(V_{\text{mss}}) - \text{MEAN}(V_{\text{Pn}} + \Psi \times V_{\text{Hz}})] / \text{MEAN}(V_{\text{mss}}) \quad (2)$$

$$\text{with } V_{\text{mss}} = V_{\text{Pn}} + V_{\text{Hz}} + V_{\text{Mgt}}, \quad (3)$$

where V is the grain volume (approximated by its surface dimensions), *mss*, *Pn*, *H_z* and *Mgt* denote monosulfide solid solution (i.e. the precursor high-T mantle sulfide), pentlandite, heazlewoodite and magnetite, respectively, and Ψ is a factor (~ 0.8) that accounts for the lower S content of heazlewoodite compared to pentlandite. This equation assumes that the amount of S loss is approximated by the difference between

the volume of the original mantle sulfide and that of residual pentlandite plus heazlewoodite. This calculation only provides first order estimates with large uncertainties (20% or more expressed as 1σ), because it assumes that mss, pentlandite and heazlewoodite have same density and does not consider the amount of heazlewoodite dispersed in serpentine veins. The calculated S losses are ~13, 60 and 76% for samples XM1/142, XM1/341 and XM1/345, respectively.

Figure 7 shows the good correlation ($r^2 = 0.999$) between calculated S loss and the difference between bulk-rock and average *in situ* $\delta^{34}\text{S}$ values for the three samples (even though we acknowledge that the statistical significance is debatable because the trend includes only 3 points). For the estimated S loss quantities, the isotopic composition of lost S is similar for the three samples (i.e. $\delta^{34}\text{S}_{\text{lost S}} = -9.2\text{‰}$ for XM1/142, -8.0‰ for XM1/341 and -6.0‰ for XM1/345). The above evidence implies that S was partially removed from these samples by similar processes. In addition, the correlation between S loss and bulk $\delta^{34}\text{S}$ variation rules out the addition (and subsequent reduction) of sulfate species during interaction with the kimberlite magma or hydrous fluids (which produced serpentinisation) as possible sources of isotopically heavy S.

The correlation between S loss and bulk $\delta^{34}\text{S}$ variation is supported somewhat by the inverse correlation between S concentrations and $\delta^{34}\text{S}$ values observed by Ionov et al. (1992) for a suite of mantle xenoliths from the Tariat basalts (Mongolia). Ionov et al. (1992) also documented that the coarse-grained fractions of some mantle xenoliths from central Asian alkali-basalts have lighter S isotope compositions than the corresponding bulk samples. This is similar to our results because for the coarse-grained fractions sulfides only occur as largely fresh inclusions in silicate minerals, whereas the bulk samples also include altered interstitial sulfides. Therefore, it

appears likely that increased bulk $\delta^{34}\text{S}$ in mantle peridotites in response to sulfide alteration is a ubiquitous process.

Partial S loss during serpentinisation is a common feature of mantle peridotites (e.g., Lorand, 1990). Serpentinisation of peridotite rocks lying at or below the seafloor may produce large variations of bulk S and corresponding deviations from initially chondritic S isotopic compositions (e.g., Alt and Shanks, 2011; Alt et al., 2013; Delacour et al., 2008). The only documented process that decreases bulk S contents while increasing bulk $\delta^{34}\text{S}$ values in oceanic peridotites during serpentinisation is kinetic fractionation during partial oxidation of mantle sulfides (Alt and Shanks, 2011; Delacour et al., 2008). Under equilibrium conditions, partial oxidation of sulfides in serpentinised peridotites would decrease the $\delta^{34}\text{S}$ compositions of residual sulfides because the sulfate products would be enriched in heavy S. However, if this process is accompanied by kinetic fractionation, the sulfate products (and S-rich compounds produced during intermediate oxidation reactions) become enriched in the lighter S isotopes, as demonstrated experimentally by Fry et al. (1988) and Grinenko and Mineyev (1992). Once the sulfate (and intermediate S-rich) compounds are removed from the system, the overall effect is decreased bulk S contents, coupled with increased bulk $\delta^{34}\text{S}$ values for the serpentinised peridotites. In this regard, Chaussidon and Lorand (1990) noted that fresh sulfide inclusions and the residual parts of partly altered (serpentinised) interstitial sulfide grains, from the same peridotite samples, have identical S isotopic compositions. These authors concluded that serpentinisation does not alter the S isotopic composition of residual mantle sulfides. We suggest that heazlewoodite, which is produced during pentlandite alteration, carries the isotopically heavier S produced by partial oxidation of pentlandite under kinetic fractionation conditions. Heazlewoodite is the most

abundant sulfide phase in samples XM1/341 and XM1/345; hence, its isotopic composition must dominate the bulk-rock signature of these xenoliths. Alternatively, alteration of pentlandite to heazlewoodite (plus magnetite) may be accompanied by isotopic fractionation under equilibrium conditions, with isotopically lighter S partitioned into the fluid phases and then removed from the system. However, no experimental or theoretical data are available to support this interpretation.

In summary, while sample XM1/142 (predominantly fresh sulfides) shows overlapping *in situ* sulfide and bulk-rock S isotope values (Fig. 6), the bulk isotopic compositions of samples XM1/341 and XM1/345 indicates modification during serpentinisation and sulfide alteration. Given that mantle peridotites are commonly affected by serpentinisation, it seems likely that both the S concentration (Lorand, 1990), and the S isotope systematics of bulk peridotite samples are often modified by alteration. This study and results presented by Ionov et al. (1992) indicate that sulfide alteration increases the bulk $\delta^{34}\text{S}$ value of peridotite rocks. It is therefore not surprising that the vast majority of bulk S isotope determinations for SCLM peridotites give $\delta^{34}\text{S} > 0\text{‰}$ (Fig. 1). This contrasts with the negative *in situ* sulfide $\delta^{34}\text{S}$ values reported here. These results seem to contradict the conclusion of Ionov et al. (1992) that the SCLM has on average positive $\delta^{34}\text{S}$ composition.

7.3. Sulfur isotope signature of the lithospheric mantle beneath Kimberley

The *in situ* S isotope analyses of metasomatised mantle xenoliths from Bultfontein show intra-grain (up to 2.7‰ $\delta^{34}\text{S}$) and within-sample variations (up to 4.4‰) that exceed the SIMS 2 σ analytical uncertainty (~0.4-0.6‰; Table S2). Previous *in situ* determinations of sulfides in mantle peridotites documented even larger variations, up

to 5.7 and 8.0‰ $\delta^{34}\text{S}$ across a single grain and rock sample, respectively (Chaussidon and Lorand, 1990; Chaussidon et al., 1989). Intra-grain variations in the current samples may be due to incomplete isotopic homogenisation during re-equilibration of high-T mss ($\pm (\text{Ni,Fe})_{3\pm x}\text{S}_2$) to pentlandite-rich assemblages possibly coupled with partial ablation of heazlewoodite ($\pm$ magnetite and/or serpentine) not exposed at surface (e.g., sample XM1/142). The wider compositional spectra of samples XM1/345 (3.3‰ $\delta^{34}\text{S}$) and DU-1 (3.5 and .4.4‰ for pentlandite and chalcopyrite, respectively) require additional explanations.

The variable major-element compositions of silicate, oxide and sulfide minerals in polymict breccia sample DU-1 (Fig. 4; Giuliani et al., 2013a, 2014b) suggests that the isotopic variability of the DU-1 sulfides may be due to incomplete equilibration of the metasomatic assemblage. Likewise, Zhang et al. (2000) documented large O isotope disequilibrium in other polymict breccia samples from the Kimberley area. This conclusion is reinforced by the indistinguishable S isotope systematics of DU-1 pentlandite and chalcopyrite (Fig. 5a,b), which derived from the same high-T Ni-Cu-rich sulfide melt (Giuliani et al., 2013a), but contrasts with the expected isotope fractionation between chalcopyrite and violarite (proxy for pentlandite) under equilibrium conditions ($\sim 1.4\text{‰}$ at $T = 200^\circ\text{C}$; Li and Liu, 2006).

For sample XM1/345, the isotopic variability in the sulfides is reflected by the variable trace element and Sr isotope systematics of LIMA and clinopyroxene (Giuliani, unpublished). Therefore, it seems likely that sample XM1/345 preserves evidence of interaction with multiple metasomatic melts of distinct isotopic composition. Similarly, Thomassot et al. (2009) and Evans et al. (2014) inferred S contributions from different sources to explain intra-sample S isotope variations for

sulfide grains included in diamonds from the Jwaneng kimberlite (Botswana) and in high-pressure metamorphic rocks from the western Alps, respectively.

The current samples show a more restricted $\delta^{34}\text{S}$ range between -5.9 and -1.0‰, with no statistically meaningful differences between samples (Fig. 5a), compared to sulfides in previously studied mantle peridotites (~-7 to +6‰; Fig. 1). The limited S isotopic variation of the Bultfontein xenolith sulfides is remarkable considering the distinct metasomatic styles and age of metasomatism for these samples (Table 1). The restricted S isotopic composition could indicate that i) the lithospheric mantle beneath Kimberley shows limited S isotope variations with $\delta^{34}\text{S}$ values between ~-6 and -1‰; ii) the sulfides equilibrated with the entraining kimberlite magma and/or post-emplacement crustal fluids; or iii) the parental metasomatic melts periodically tapped a source with limited S isotope variability.

The first hypothesis is not consistent with the isotope systematics ($\delta^{34}\text{S} = -4$ to +3‰; Eldridge et al., 1991) of sulfide inclusions in peridotitic diamonds from the Kimberley area (Koffiefontein, Jagersfontein, Finsch, Roberts Victor – Fig. 2). Magmatic sulfides in kimberlites investigated thus far have $\delta^{34}\text{S}$ values between -0.1 and +2.5‰ (Fig. 1; Giuliani et al., 2014a). Therefore, isotopic equilibration with kimberlite melts would produce circa-chondritic S isotope compositions, clearly distinct from the observed range. Interaction with hydrous fluids after kimberlite emplacement may have contributed to the scatter of S isotope values, but not their homogenisation. Indeed, the *in situ* analyses of sulfides displaying different degrees of alteration (i.e. XM1/142 vs XM1/345) and, therefore, interaction with hydrous fluids, produce similar results (average $\delta^{34}\text{S} = -4.2 \pm 1.0$ vs -4.4 ± 1.2 ‰ (1sd), respectively). Our preferred interpretation is that metasomatic fluids operating

beneath Kimberley at ~180 and 90-80 Ma were sourced from a reservoir with limited S isotope variations.

Recent studies of mid-ocean ridge basalts (MORB) by Labidi et al. (2012, 2013, 2014) revealed that the asthenospheric mantle has a $\delta^{34}\text{S}$ signature $< 0\text{‰}$ and, more probably, $\leq -1.4\text{‰}$. Therefore, the asthenospheric mantle is a possible source of S for the metasomatic melts. However, the isotopic composition of sulfides in the Bultfontein xenoliths extends to $\delta^{34}\text{S}$ values of -5.9‰ , which requires another S source(s). Sulfide grains in mantle eclogites and eclogitic diamonds show large $\delta^{34}\text{S}$ deviations from 0‰ (Fig. 1), which are attributed to the occurrence of recycled crustal S in the Earth's mantle (Eldridge et al., 1991; Thomassot et al., 2009). It is therefore likely that some S of crustal origin was present in the source of the metasomatic melts that affected the Bultfontein xenoliths.

The main contributor of S in subducted slabs is the oceanic crust with about 5/6 provided by the variably altered igneous section and 1/6 by the sedimentary cover (Alt et al., 2013). The altered upper (volcanic) section of the oceanic crust is characterised by negative $\delta^{34}\text{S}$ values (e.g., Alt and Shanks, 2011) and, once subducted, could represent a possible S source for the metasomatic fluids. However, this hypothesis is not favoured because the S isotope profile across an entire section of oceanic crust reveals that the $\delta^{34}\text{S}$ signature of the altered igneous sector ($\sim -0.9\text{‰}$; Alt, 1995) is close to chondritic values. The sedimentary record shows large S isotopic variations for both seawater sulfates ($\delta^{34}\text{S} \geq 5\text{‰}$) and sedimentary pyrite through time (Fig. 1). Sedimentary pyrite exhibits predominantly positive $\delta^{34}\text{S}$ values until ~500 Ma and largely negative values thereafter (e.g., Farquhar et al., 2010). In this regard, Canfield (2004) proposed that a sulfur reservoir with negative $\delta^{34}\text{S}$ signature is missing in the Archean-Proterozoic sedimentary record and could have been

subducted and stored in the Earth's mantle. It is important to note that studies of high-P and high-T metamorphic rocks have shown that S isotope compositions are not modified by prograde metamorphism (Cook and Hoefs, 1997; Evans et al., 2014 and references therein) and that S is partially retained and transferred into the mantle during high-P metamorphism of subducted rocks (Alt et al., 2013; Evans et al., 2014). We therefore propose that the metasomatic melts, which affected the Bultfontein xenoliths, originated from a source containing subducted sediments with negative $\delta^{34}\text{S}$ compositions. These sediments could represent the missing sedimentary reservoir implied by Canfield (2004). Subducted sediments, with distinct S isotopic compositions (i.e. $\delta^{34}\text{S} < \text{and} > 0\text{‰}$, respectively), are suggested to occur in the source(s) of ocean island basalts (OIB) from Mangaia (Polynesia; Cabral et al., 2013) and Samoa (Labidi et al., 2015).

Sulfide inclusions in olivine from the Mangaia lavas also show $\Delta^{33}\text{S} \neq 0 (\pm 0.2)\text{‰}$, which indicates an Archean age for the recycled sediments (Cabral et al., 2013). Sulfur with significant MIF (i.e. $\Delta^{33}\text{S} \neq 0 \pm 0.2\text{‰}$) was also identified in sulfide inclusions from eclogitic diamonds (Farquhar et al., 2002; Thomassot et al., 2009) and interpreted to reflect incorporation of Archean, surface-derived S in the mantle. Our *in situ* analyses of sulfides do not show any evidence of MIF, which may be partly due to the large analytical uncertainties associated with SIMS analyses ($\pm 0.2\text{-}0.4\text{‰}$ $\Delta^{33}\text{S}$; Table S2). In fact, the bulk analysis of sample XM1/341 reveals a $\Delta^{33}\text{S}$ value ($0.079 \pm 0.016\text{‰}$) that deviates slightly from the chondritic value. In contrast, the S isotopic compositions of other samples are similar to, or within uncertainty of 0‰ and plot in the $\Delta^{33}\text{S}$ range of MORBs (-0.005 to $+0.011\text{‰}$; Labidi et al., 2012, 2013, 2014). Assuming that alteration of XM1/341 sulfides did not affect their $\Delta^{33}\text{S}$ values and the MORB range is representative of the asthenospheric mantle,

the S isotopic composition of sample XM1/341 indicates that recycled crustal S was present in the source of the metasomatic melt that affected this xenolith. $\Delta^{33}\text{S}$ deviates significantly from 0‰ in sedimentary and volcanic rocks only before ~2.4 Ga (e.g., Farquhar and Wing, 2003); however, variations between -0.15 and +0.34‰ are documented after 2.4 Ga (Farquhar et al., 2010 and references therein). Therefore, the small MIF shown by sample XM1/341 does not provide any constraint on the age of the S-bearing recycled material.

8. Conclusions

This combined *in situ* sulfide and bulk-rock S isotope investigation of metasomatised mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa) provides new insights into the processes affecting the S isotope composition of mantle sulfides after their crystallisation in the mantle. Mass balance calculations show that re-equilibration of high-T mantle sulfides ($\text{mss} \pm (\text{Ni,Fe})_{3\pm x}\text{S}_2$) to low-T pentlandite-rich assemblages is accompanied by limited isotopic fractionation. Therefore, the isotope systematics of pentlandite are broadly representative of the parental metasomatic melt. Conversely, increasing rates of sulfide alteration and S removal during peridotite serpentinisation, fractionate the S isotopes between mantle sulfides and alteration products with an increase of the $^{34}\text{S}/^{32}\text{S}$ ratio in bulk peridotites. Bulk determinations of the S isotope composition of mantle peridotites are only representative of the mantle values if the sulfides are predominantly fresh. An important implication of this study is that previous bulk-rock determinations of mantle peridotite xenoliths, which are dominated by positive $\delta^{34}\text{S}$ values, require revision.

Sulfides in the Bultfontein xenoliths exhibit limited S isotope variations of between -5.9 and -1.0‰ $\delta^{34}\text{S}$ despite of the variable style and age of metasomatic enrichment recorded by the samples. Our preferred interpretation is that metasomatic fluids operating beneath Kimberley at ~180 and 90-80 Ma were sourced from a reservoir with limited S isotope variations. The low $^{34}\text{S}/^{32}\text{S}$ composition of sulfides in the Bultfontein xenoliths suggest that the fluid source was probably located in the asthenospheric mantle and contained recycled crustal S of sedimentary origin.

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Figure captions

Figure 1. Sulfur isotope ($\text{‰ } \delta^{34}\text{S}$ relative to VCDT) variations in marine sulfates (Farquhar et al., 2010 and references therein), sedimentary pyrite (Farquhar et al., 2010 and references therein), ocean island basalts (OIBs – Cabral et al., 2013; Chaussidon et al., 1989; Labidi et al., 2015), mid-ocean ridge basalts (MORBs – Labidi et al., 2012, 2013, 2014), bulk peridotite xenoliths entrained in the sub-continental lithospheric mantle (SCLM) by kimberlite and alkali-basalt magmas (Ionov et al., 1992; Kyser, 1990; Wilson et al., 1996), sulfides in SCLM peridotites (Chaussidon and Lorand, 1990; Chaussidon et al., 1989; Tsai et al., 1979) and in diamonds of peridotitic and eclogitic paragenesis (Eldridge et al., 1991; Cartigny et al., 2009; Chaussidon et al., 1987; Farquhar et al., 2002; Rudnick et al., 1993; Thomassot et al., 2009), sulfides in SCLM eclogite xenoliths sampled by kimberlite magmas (Chaussidon et al., 1989; Rudnick et al., 1993; Tsai et al., 1979; Vinogradov and Ilupin, 1972), and magmatic sulfides in kimberlites (Giuliani et al., 2014a and references therein).

Figure 2. Schematic map of southern Africa showing the location of the Kimberley cluster of kimberlites. The estimated boundary of the Kaapvaal craton and the location of major kimberlite and orangeite intrusions in the Kimberley area are also shown (RoVic = Roberts Victor).

Figure 3. Photomicrographs (a, c, h) and SEM-EDS images (b, d, e, f, g, i) of sulfide minerals in Bultfontein mantle xenoliths. a) XM1/142: pentlandite (Pn) grain associated with clinopyroxene (Cpx), spinel (Spl) and phlogopite (Phl). b, c)

XM1/142: micro-textures of pentlandite grains: (b) ‘Rods’ and ‘blades’ of Ni-rich pentlandite (Ni-Pn), and highly fractured domains of Fe-rich pentlandite (Fe-Pn); (c) minute ($<10\ \mu\text{m}$) segregations of magnetite (Mgt) in a pentlandite grain traversed by abundant serpentine veins (not labelled). d) XM1/341: fractured inclusion of pentlandite ($\pm$ magnetite) in clinopyroxene. e, f) XM1/341: aggregate of microporous magnetite and homogeneous, inclusion-free heazlewoodite after pentlandite; magnetite hosts abundant micron-sized inclusions of heazlewoodite. g) XM1/345: pentlandite remnant in interstitial aggregate of magnetite $\pm$ heazlewoodite. h, i) DU-1: sulfide segregation and (i) detail showing intergrown pentlandite and chalcopyrite (Cp), the latter being partly replaced by Cu sulfide (CuS). Ol: olivine; Ilm: ilmenite.

Figure 4. Co-variation plots of Ni/Fe atomic ratio vs (a) S (wt.%), (b) O (wt.%), (c) Co (atomic %) and (d) Cu (atomic %); and (e) atomic S – Fe – Ni+Co ternary plot for sulfide grains in Bultfontein mantle xenoliths. In panel (e), the $\sim 900^\circ\text{C}$ phase boundaries for high-temperature monosulfide solid solution (mss), Ni-rich sulfide liquid and 2-phase field from Craig and Kullerud (1969) are superimposed. Note that measured pentlandite compositions are not stable at these conditions.

Figure 5. *In situ* sulfur isotope ($\text{‰}\ \delta^{34}\text{S}$ relative to VCDT) analyses of (a) pentlandite and (b) chalcopyrite grains in Bultfontein mantle xenoliths; (c) SEM-EDS image of sulfide grain in sample XM1/345 showing $\delta^{34}\text{S}$ variations (as ‰ units) measured by SIMS. Values reported in yellow represent mixtures of pentlandite and heazlewoodite and are not considered quantitative because the instrumental fractionation factor for heazlewoodite is unknown. Mgt: magnetite; Hz: heazlewoodite.

885 **Figure 6.** Comparison between the $\delta^{34}\text{S}$ (‰ relative to VCDT) and $\Delta^{33}\text{S}$ (‰) values
886 of average *in situ* sulfide analyses and bulk-sample measurements. Error bars
887 represent 1sd (standard deviation) for average *in situ* analyses and external
888 reproducibility for bulk determinations. For sample DU-1 the *in situ* analyses of
889 pentlandite (Pn) and chalcopyrite (Cp) are plotted using separate symbols. For sample
890 XM1/341 only one *in situ* analysis was obtained. Dotted lines join *in situ* sulfide and
891 bulk-rock determinations for the same xenolith sample. Note that the *in situ* sulfide
892 and bulk-rock $\delta^{34}\text{S}$ values are only coincident for sample XM1/142.

893

894 **Figure 7.** Relationship between estimated S loss (wt.%) and the difference between
895 $\delta^{34}\text{S}$ (‰ relative to VCDT) values of bulk-rock versus average *in situ* sulfide analyses
896 for samples XM1/142, XM1/341 and XM1/345. Only one *in situ* analysis was
897 obtained from sample XM1/341. A linear regression through the 3 points returns a R^2
898 value of 0.999.

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