1 **Mantle oddities: A sulphate fluid preserved in a MARID xenolith**
2 **from the Bultfontein kimberlite (Kimberley, South Africa)**

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20 Abstract: 314 words

21 Text: 6270 words

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Abstract

Sulphur in the lithospheric mantle is concentrated in sulphide minerals, with limited evidence for the occurrence of sulphate phases. Here we describe an unusual assemblage of celestine (SrSO_4), clinopyroxene and minor phlogopite, pectolite, sphene, apatite, barite (BaSO_4) and Ca-Sr carbonates in a MARID mantle xenolith sampled by the Bultfontein kimberlite (Kimberley, South Africa). This assemblage occurs in veins that pervasively traverse the xenolith, indicating that celestine and the other vein minerals crystallised from a fluid. In the MARID host rock, K-richterite is resorbed where in contact with celestine and is overgrown by clinopyroxene. Celestine hosts the other metasomatic vein phases, but also occurs as inclusions in euhedral clinopyroxene, suggesting co-precipitation of these minerals. Celestine was partly replaced by serpentine during alteration by hydrous fluids after kimberlite emplacement in the upper crust. Celestine has relatively radiogenic Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70677$), which overlap those of K-richterite in the MARID host rock and fall within the range of other MARID and phlogopite–K-richterite peridotites sampled by southern African kimberlites. Celestine displays S isotopes ($\delta^{34}\text{S} = +5.9\%$) that are slightly heavier than typical mantle values ($\delta^{34}\text{S} \sim 0\%$) and there is no evidence of mass-independent fractionation ($\Delta^{33}\text{S} = -0.01\%$).

The texture and chemical composition of the metasomatic phases indicate that the MARID rock was infiltrated by a sulphate fluid enriched in Sr, Ba, Na and Ca, with lesser P, Ti, LREE, CO_2 and F. The similar Sr/Ba ratios and Sr isotopic compositions of celestine and K-richterite suggest that K-richterite breakdown contributed to the alkali enrichment of the sulphate fluid. A mantle origin for the sulphate fluid is supported by i) comparisons between the Sr-S isotopic compositions

of celestine and the host kimberlite, crustal and mantle lithologies from the area, and
ii) alteration of celestine by late-stage hydrous fluids. Consequently, the celestine-
bearing veins provide the first clear evidence for the occurrence of sulphate-
dominated fluids in the Earth's mantle.

Keywords: sulphate fluid, S–Sr isotopes, metasomatism, lithospheric mantle,
kimberlite

1. Introduction

Sulphur is the eleventh most abundant element in the silicate Earth, with a
primitive mantle concentration estimated as 250 ppm (McDonough and Sun, 1995).
Sulphur is a moderately incompatible volatile element that plays a pivotal role in
transporting and concentrating chalcophile metals. In this regard, sulphide melts are
enriched in metallic elements (e.g. Lorand et al., 2004; Alard et al., 2011) and
sulphide and bisulphide anions complex with metallic cations dissolved in C-O-H-S
fluids. By studying S-bearing minerals in mantle rocks, it is possible to improve our
understanding of sulphur distribution and speciation in the mantle. This has important
implications for the formation of melts enriched in S and metals, which are ultimately
involved in generating magmatic ore deposits (Fiorentini and Beresford, 2008;
Tomkins et al., 2012).

In the sub-continental lithospheric mantle (SCLM), sulphur is mainly stored in
sulphide minerals in the reduced form S^{2-} . Mantle sulphides may have originated from
immiscible sulphide melts that separated from silicate and/or carbonate melts at

mantle depth (Giuliani et al., in press-a; Kogarko et al., 1995; Lorand et al., 2004), from S-bearing C-O-H fluids (Giuliani et al., 2013), and from sulphidation reactions between S-bearing fluids and silicate minerals (Lorand and Grégoire, 2006). It has also been proposed that some sulphide minerals could be residual after the partial melting events that stabilised the lithospheric roots of continents (Griffin et al., 2004).

In addition to sulphides, sulphur in the SCLM may also occur in the oxidised form SO_4^{-2} , in minerals such as apatite and amphibole, albeit in trace amounts. In addition, anhydrite (CaSO_4) has been reported as inclusions in diamond (Leung, 1990), barite (BaSO_4) in Cr-diopside from a peridotite xenolith (Hervig and Smith, 1981), and alkali-rich sulphates in carbonate-rich inclusions hosted by ilmenite in a mantle polymict breccia (Giuliani et al., 2012). These occurrences attest to the presence of sulphate minerals in the mantle, even at depths within the diamond stability field (> 150 km). ‘Daughter’ crystals of gypsum and barite have been reported from fluid inclusions hosted by mantle olivine, pyroxene and amphibole (Frezzotti et al., 2012; Konzett et al., 2000); this suggests that SO_3 may be a more common component of some mantle fluids than previously recognised. The occurrence of sulphate compounds in mantle fluids is further supported by mass spectrometric analyses of crushed mantle xenoliths from south-eastern Australia, which showed the release of SO_2 during crushing (O’Reilly et al., 1990). Finally, sulphates have been identified in metasomatised rocks from mantle wedge zones above subduction zones, which are permeated by sulphate-rich oxidising melts (McInnes and Cameron, 1994; Metrich et al., 1999; Tomkins et al., 2012).

Sulphates can crystallise from a range of chemically different fluids (throughout the paper, we use the term ‘fluid’ to include ‘melts’ as well as C-O-H-S ‘fluids’ with dissolved silicate or carbonate components – Harte, 1987). Sulphates are

common constituents of carbonatitic rocks. Anhydrite has been shown to crystallise from silicate magmas of intermediate to acid composition (Bart and Dorais, 2008; Chamberfort et al., 2008; Luhr, 1990). Sr-rich barite and less common alkali-sulphate minerals occur in the groundmass of kimberlites (Mitchell, 1994; Kamenetsky V. et al., 2007). Celestine (SrSO_4) and apthitalite $[(\text{K},\text{Na})_3\text{Na}(\text{SO}_4)_2]$ have been found in melt inclusions hosted by kimberlitic olivine (Mernagh et al., 2011). Barite is a minor constituent of vein assemblages documented from mantle MARID (mica-amphibole-rutile-ilmenite-diopside) rocks and may have crystallised from kimberlite-related fluids (Dawson and Smith, 1977; Grégoire et al., 2002; Waters, 1987).

There is also evidence for the occurrence of sulphate fluids in crustal rocks and documentation of sulphate melts from experimental simulations. Panina and Motorina (2007 and references therein) and Naumov et al. (2008 and references therein) reported evidence of immiscible alkali-sulphate melt droplets included in magmatic minerals from alkaline basic and ultrabasic complexes around the world. Droplets of Sr-barite, included in clinopyroxene megacrysts hosted by alkali basalts, were interpreted as immiscible sulphate melts from the lower crust ($P \sim 10$ kbar; Torok et al., 2003). Jugo et al. (2005) and Martin et al. (2012) demonstrated that sulphate and sulphate-carbonate melts could be generated from liquid-state immiscibility of parental S- and S- CO_2 -rich basaltic melts at 10 kbar. Nonetheless, despite increasing evidence for the occurrence of sulphate melts in crustal rocks, such fluids have never been documented in mantle rocks.

In this contribution we report the occurrence of Ba-bearing celestine veins that also host abundant clinopyroxene and minor sphene, apatite, pectolite, phlogopite, barite and carbonates, in a mantle MARID xenolith (XM1/498) sampled by the Bultfontein kimberlite (Kimberley, South Africa). We provide textural, mineral

inclusion, mineral chemical, and Sr plus S isotope data on celestine and the other minerals in sulphate veins as well as the host MARID minerals. Our results suggest that the sulphate-rich veins were produced in the mantle from interaction between a sulphate-rich fluid and the MARID host rock.

1.1. Geological background

The Bultfontein kimberlite is one of four major diamond-producing kimberlites in the Kimberley cluster (Phillips et al., 2004), located in the south-eastern part of the Kaapvaal craton (Field et al., 2008). The Kimberley kimberlites are classified as Group I kimberlites on the basis of their Sr-Nd isotope signatures (Smith, 1983). Emplacement of these kimberlites has been dated at 81 to 90 Myr, using various isotopic systems (e.g. phlogopite Rb/Sr - Allsopp and Barrett, 1975; Kramers et al., 1983; zircon U/Pb - Davis, 1977; phlogopite $^{40}\text{Ar}/^{39}\text{Ar}$ - Fitch and Miller, 1983). The Kimberley kimberlites are well known for hosting a variety of mantle xenoliths, characterised by distinct metasomatic styles (Erlank et al., 1987; Grégoire et al., 2002; Pearson et al., 2003).

1.2. MARID rocks

MARID rocks are phlogopite-rich mantle xenoliths sampled by kimberlite magmas. MARID rocks host variable amounts of K-richterite amphibole and diopside, and lesser quantities of ilmenite and rutile (Dawson and Smith, 1977). K-richterite or diopside may be absent from the primary MARID assemblage (Dawson and Smith, 1977; Waters, 1987). The formation of MARID rocks has been attributed

to crystallisation from alkali-rich melts such as lamproites (Waters, 1987), Group I (Dawson and Smith, 1977) and Group II kimberlites (Grégoire et al., 2002; Konzett et al., 1998), or to metasomatic conversion of refractory mantle peridotite by kimberlite melts (Choukroun et al., 2005).

Secondary mineral assemblages in veins and patches are frequently documented in MARID rocks, and include calcite, clinopyroxene (usually euhedral forms) and phlogopite; K-richterite amphibole, apatite, sphene, barite and other exotic minerals are sometimes also observed (Dawson and Smith, 1977; Grégoire et al., 2002; Waters, 1987). The compositions of clinopyroxene, phlogopite and K-richterite occurring in these late-veins differ from the primary MARID minerals (Dawson and Smith, 1977; Waters, 1987). These vein assemblages formed after MARID metasomatism, either immediately prior to or during xenolith entrainment by the kimberlite magma, and are probably related to infiltration of kimberlite or other mantle fluids (Dawson and Smith, 1977; Waters, 1987). In contrast, we will show the vein assemblage described here represents a primary alteration assemblage that formed in the mantle after MARID metasomatism, but before kimberlite magmatism.

2. Analytical Methods

Thin sections of MARID xenolith XM1/498 were characterised under transmitted and reflected light using a Nikon Labophot 2-Pol petrographic microscope. The textural relationships and compositions of the phases were then investigated in detail using a Scanning Electron Microscope (SEM) and Electron Microprobe (EMP). A preliminary study of xenolith microstructures was performed on carbon coated thin sections at the University of Melbourne, using a Philips (FEI)

XL30 ESEM TMP, equipped with an OXFORD INCA energy-dispersive X-ray spectrometer (EDS). For more detailed investigation of the sulphate-rich veins, the thin sections were examined at the Central Science Laboratory, University of Tasmania, using a Hitachi SU-70 field emission scanning electron microscope (FE-SEM) equipped with an OXFORD INCA-XMax80 EDS. The FE-SEM provides ultra-high resolution imaging, which enables examination of nm-sized surface features in secondary electron mode. A beam acceleration voltage of 15 kV was employed during the acquisition of X-rays for semi-quantitative chemical analyses using both the SEM and FE-SEM.

Electron microprobe and LA-ICP-MS analyses were then undertaken to determine the chemical compositions of minerals in thin section. Major oxide analyses were performed using the University of Melbourne Cameca SX-50 Electron Microprobe, which is equipped with four vertical Wavelength Dispersive Spectrometers. The analytical conditions were: beam acceleration voltage of 15 kV, beam current of 35/25 nA, and beam diameter of 2 μm ; counting times per analysis of 20 seconds on peak positions and 10 seconds on two background positions located on either side of the peak position; detection limits of ~ 300 ppm for most elements.

In-situ trace element analyses were performed using a HELEX excimer (193 nm) UV laser ablation system interfaced with a Varian 810 quadrupole ICP-MS located at the University of Melbourne (Woodhead et al., 2007). Laser ablation conditions for the current study were as follows: ablation times between 50 and 60 s; repetition rate of 5 Hz; standard delay for sample washout of 20-30 seconds; longer delays for background measurements (60 seconds) every 8-10 analyses, and at the beginning and end of each analytical session; laser spot size of 32, or 42 μm depending on crystal size. Internal standardisation was achieved using ^{29}Si (for

phlogopite and pectolite), ^{43}Ca (for K-richterite and clinopyroxene) and ^{88}Sr (for celestine). NIST612 and BCR2-G glasses were used for calibration, and BHVO-2G and NIST610 glasses were analysed as unknowns to verify data integrity.

2.1. Strontium isotopes

In-situ Sr isotopic analyses of celestine and K-richterite were performed using the same laser ablation system employed for trace element analyses, interfaced with a NU Plasma MC-ICP-MS. The laser ablation conditions were as follows: for celestine ablation time of 60 s, repetition rate of 1 Hz; beam size of 19 μm ; for K-richterite ablation time of 50 s, repetition rate of 5 Hz; beam size of 120 μm ; standard delay for sample washout of 30 seconds; longer delays of 60 seconds for background measurements every 15 analyses, and at the beginning and end of each analytical session. Typical signal sizes on Faraday collectors were 7.5-9.0 V of total Sr for celestine, and ~ 0.7 V for K-richterite. The raw data were reduced using the in-house IOLITE software, which applies corrections for the main isobaric interferences (e.g. ^{87}Rb on ^{87}Sr , doubly-charged Er and Yb on $^{84,86,88}\text{Sr}$ and ^{85}Rb – Paton et al., 2007; Woodhead et al., 2005). Fragments of modern marine carbonate (nominal $^{87}\text{Sr}/^{86}\text{Sr} = 0.70916$; Woodhead et al., 2005), and perovskite 83P13 from the Tummatapalle kimberlite (nominal $^{87}\text{Sr}/^{86}\text{Sr} = 0.70250$; Paton et al., 2007) were used to initialise the instrument and correct for analytical bias. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured for these standards (carbonate: 0.70913 ± 0.00018 [1σ], $n=7$; perovskite: 0.70239 ± 0.00012 , $n=8$) are consistent with accepted values.

Isotope dilution Rb-Sr data were collected for two samples of K-richterite. The handpicked separates (~ 6 mg) were cleaned with cold, dilute HCl and distilled water,

spiked with an ^{85}Rb - ^{84}Sr tracer and dissolved in HF-HNO₃ and HCl on a hot plate (100°C) over 3-4 days. Rubidium and Sr were extracted and purified using a combination of conventional cation resins and Eichrom Sr resin (Maas et al., 2005). Isotopic analyses were carried out on a NU Plasma MC-ICP-MS operated with a low-uptake desolvating device (Maas et al., 2005), using an analytical set-up similar to that used for laser ablation Sr isotope analyses (Woodhead et al., 2005). Strontium isotopic data were acquired with total Sr signals near 8 V and corrected for instrumental mass bias by normalizing to $^{88}\text{Sr}/^{86}\text{Sr} = 8.37521$, using the exponential law as part of an online iterative spike unmixing procedure. Data are reported relative to SRM987 = 0.710230 and have an internal precision of ± 0.000020 (2σ). Rubidium isotope dilution analyses were carried out using the Zr-doping method. A split of USGS basalt BCR-2, processed and analysed in the same batch, yielded $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.397 ± 0.001 and 0.705021 ± 0.000019 (2σ) respectively, consistent with TIMS reference data (e.g. Maas and McCulloch, 1991; Raczek et al., 2000, 2003). Based on the long-term reproducibility for rock standards, the external precision (2σ) for $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ are estimated to be better than $\pm 0.5\%$ and $\pm 0.006\%$, respectively.

2.2. Sulphur isotopes

Sulphur isotopic values ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$) are reported in the conventional δ notations with respect to VCDT (Vienna-Canon Diablo Troilite) defined as $\delta^x\text{S} = 1000 \times [({}^x\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^x\text{S}/{}^{32}\text{S})_{\text{VCDT}} - 1]$, where x is 33, 34 and 36, respectively. Most physical and chemical processes fractionate S isotopes according to the mass difference between the isotopes. However, the S isotopes of several Archean rocks

deviate from the mass-dependant fractionation trend, and display mass-independent fractionation (e.g. Farquhar et al., 2007; Philippot et al., 2012). $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are measures of mass-independent fractionation of the S isotopes, and are defined as $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1]$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{1.91} - 1]$ (Farquhar and Wing, 2003).

The S isotopes of celestine separates were measured in the Stable Isotope Laboratory of the Department of Earth and Planetary Sciences, McGill University. About 2 mg of hand-picked pure celestine were crushed, and S from the resulting powder was extracted using a Thode reagent and reacted to Ag_2S . The resulting Ag_2S was fluorinated at 225°C in a Ni bomb under ~20X stoichiometric excess F_2 for more than 9 h. The SF_6 produced was purified cryogenically and chromatographically and analyzed on a Thermo Electron MAT 253 mass spectrometer for multiple sulfur isotope measurements in a dual-inlet mode. The precision (1σ) on individual measurements is better than 0.05‰ for $\delta^{34}\text{S}$ values, 0.01‰ for $\Delta^{33}\text{S}$ values, and 0.1‰ for $\Delta^{36}\text{S}$ values. Accuracy of the measurements is controlled by the analytical reproducibility (1σ), which for the full measurement procedure is better than 0.1‰ for $\delta^{34}\text{S}$ values, 0.01‰ for $\Delta^{33}\text{S}$ values, and 0.2‰ for $\Delta^{36}\text{S}$ values. Repeat analyses of the international reference materials IAEA-S-1, IAEA-S-2, and IAEA-S-3 match accepted values within these uncertainties.

3. Results

3.1. Sample description

Xenolith sample XM1/498 is a small (approximately 3×3×2 cm) off-cut (Fig. 1) from a larger sample of MARID rock. The sample displays a coarse grained (1 to 4 mm), anisotropic texture and consists of alternate layers enriched in K-richterite amphibole and phlogopite, respectively. Ilmenite and rutile are minor constituents of the sample (< 5-10 vol.%). Creamy-coloured veins of Ba-bearing celestine (Figs. 1, 2a), with subordinate clinopyroxene (Fig. 2b), pervasively traverse the K-richterite-rich layers. Another peculiar feature of the K-richterite-rich layers is the occurrence of large ($\leq$ 3-4 mm) pools of celestine, which host abundant clinopyroxene and up to 600 μm -sized aggregates of phlogopite and pectolite [$\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$] (Fig. 2c). K-richterite is resorbed where in contact with celestine (Fig. 2d).

3.2. Petrography of sulphate-rich veins

Celestine is the most abundant constituent of the sulphate-rich veins (approximately 60-70 vol.%). Celestine occurs as tabular grains (up to 250 μm in size) and shows a lamellar structure, with alternating bands exhibiting different back-scattered electron (BSE) responses due to different Ba contents (Fig. 2e). In the sulphate-rich veins and pools, clinopyroxene is the second most abundant phase (10-20 vol.%) and forms euhedral grains (up to 200 μm) that commonly overgrow pre-existing K-richterite (Fig. 2d). Thus, relicts of K-richterite are commonly preserved as inclusions in clinopyroxene (Fig. 2b). Clinopyroxene also hosts small ($\leq$ 5 μm) inclusions of celestine, sphene, apatite, calcite, emmonite (or Ca-rich strontianite [(Sr,Ca)CO₃]) and Fe-Cr-Ti spinel (Fig. 2d and Figs. 1EA-2EA in Supplementary Material). Celestine is the most common inclusion, often exhibits a rounded shape and occurs as single isolated grains in either the core or rim of clinopyroxene.

Clinopyroxene hosts fractures containing celestine; however in some cases, celestine veinlets are entirely enclosed in the clinopyroxene host (Fig. 1EA in Supplementary Material). Small grains ($\leq 30 \mu\text{m}$) of phlogopite, sphene, pectolite and apatite commonly occur in the sulphate-rich veins, whereas emmonite and Sr-bearing barite are less common. Sphene also occurs as thin rims around ilmenite grains.

The grain boundary contacts between celestine and the silicate and oxide minerals in the veins, are usually straight and faceted (e.g. Fig. 2b, d, e). However, inter-grain boundaries between celestine and other minerals, particularly K-richterite commonly contain thin films of a Mg-Fe silicate (probably serpentine). High magnification examination with FE-SEM reveals that serpentine has replaced celestine along grain margins and cleavage planes (Fig. 2f), producing a porous texture (Fig. 2g, h). In more intensely serpentinised areas of the sulphate-rich veins, phlogopite is replaced by chlorite and apatite by serpentine (Fig. 3EA in Supplementary Material).

3.3. Mineral chemistry

The major oxide and trace element compositions of K-richterite and phlogopite in sample XM1/498 are in the range of MARID minerals analysed previously (Figs. 3 and 4; Grégoire et al., 2002; Waters, 1987), and are indistinguishable from the data reported by Konzett et al. (1998) for another off-cut of the same sample. The K-richterite has a relatively homogeneous composition with no core-rim variations, even where partially replaced by clinopyroxene. The average CaO content of K-richterite is $6.4 (\pm 0.2 [1\sigma])$ wt.% (Table 1), whereas Sr varies

between 643 and 731 ppm and Ba between 19 and 52 ppm ($\text{Sr/Ca} = 1.51 \pm 0.04 \times 10^{-3}$; $\text{Sr/Ba} = 22 \pm 7$; Table 2 and Fig. 5).

The coarse phlogopite grains in the xenolith have the same composition (within analytical uncertainty) as phlogopite in the sulphate-rich veins and pools. Phlogopite exhibits high Mg# (85.0 ± 0.3) and moderately high TiO_2 contents (1.09 ± 0.08 wt.%), but low Cr_2O_3 abundances (< 0.15 wt.%; Table 1). Calcium, Sr and Ba contents (measured by laser ablation ICP-MS) of coarse phlogopite grains range between 96 - 225, 5 - 35 and 423 - 559 ppm, respectively ($\text{Sr/Ca} = 0.08 \pm 0.04$; $\text{Sr/Ba} = 0.04 \pm 0.02$; Table 2 and Fig. 5). No LA-ICPMS measurements were carried out on phlogopite from the sulphate veins because of the small grain size ($\leq 30 \mu\text{m}$).

The concentrations of SrO and BaO in celestine are highly variable (40.2 - 56.2 and 0.03 - 17.7 wt.%, respectively, Table 1), which is consistent with the observed variations in BSE response (Fig. 2e). The inverse correlation between celestine Sr and Ba contents (Fig. 3a) reflects the solid solution between celestine and barite. However, the $(\text{Sr,Ba})\text{SO}_3$ solid solution shows a miscibility gap at intermediate compositions (Hanor, 2000), which may explain the occurrence of rare barite grains in the sulphate-rich veins. Celestine has low CaO and Na_2O contents (≤ 0.5 and 0.05 wt.%, respectively), and extremely low REE concentrations (Table 2), aside from Eu (≤ 1.31 ppm) and La (≤ 0.39 ppm).

The composition of clinopyroxene is variable between different grains and within single grains, but without any systematic core-rim zoning. For example, FeO ranges from 3.5 to 6.1 wt.%, Na_2O from 0.5 to 1.7 wt.%, and TiO_2 from 0.5 to 1.2 wt.% (Table 1). Major oxide co-variation diagrams show that the compositional variations of clinopyroxene are not related to the replacement of K-richterite or to diffusion from adjacent K-richterite (Fig. 3b). The clinopyroxene grains in the

346 sulphate-rich veins of xenolith XM1/498 show higher MgO, TiO₂, Ni, Nb and HREE
347 and lower SiO₂ and Pb than typical MARID diopside (Figs. 3c and 4c; Grégoire et al.,
348 2002; Waters, 1987).

349 Among the other phases in the sulphate-rich veins and pools, sphene displays
350 complex compositional zonation with respect to Ti, Ca and Fe (Table 1), with Ti and
351 Fe being inversely correlated (Fig. 4EA in Supplementary Material). The composition
352 of pectolite is close to stoichiometric [NaCa₂Si₃O₈(OH)], with only minor FeO (≤ 0.5
353 wt.%) present (Table 1); pectolite is relatively enriched in Sr (~500 ppm; Table 2).
354 Semi-quantitative EDS analyses (Table 1EA in Supplementary Material) show that
355 the apatite grains in the sulphate-rich veins, as well as apatite inclusions in
356 clinopyroxene, are enriched in Na₂O (2.0-4.3 wt.%), F (1.5-2.5 wt.%) and SO₃ (up to
357 2.0 wt.%), with some grains containing high levels of SrO, BaO and Ce₂O₃ (up to
358 12.3, 5.0 and 2.7 wt.%, respectively).

360 3.4. Sr isotopes

362 *In-situ* isotopic analyses of celestine yield a weighted mean ⁸⁷Sr/⁸⁶Sr ratio of
363 0.70677 ± 0.00005 (2 σ , n=9; Table 3), and ⁸⁷Rb/⁸⁶Sr $\leq 1.2 \times 10^{-4}$. Due to the low Rb/Sr
364 ratio, age corrections are minimal and calculated initial ⁸⁷Sr/⁸⁶Sr ratios at 84 Myr
365 (emplacement age of the Bultfontein kimberlite – Allsopp and Barrett, 1975; Kramers
366 et al., 1983) are indistinguishable from the measured ratios. The celestine ⁸⁷Sr/⁸⁶Sr
367 value is within the range for minerals from MARID and phlogopite–K-richterite
368 peridotite xenoliths from the Kaapvaal craton (Fig. 6), but is distinctly higher than
369 that recorded from southern African Cretaceous Group I kimberlites, including the

Kimberley kimberlites (perovskite: 0.70449 - 0.70461; Woodhead et al., 2009 – Fig. 6).

Attempts to measure the Sr isotope compositions of other Sr-bearing minerals from xenolith XM1/498 (e.g. clinopyroxene, K-richterite, phlogopite) were complicated by the ubiquitous presence of celestine impurities. For this reason, Rb-Sr isotopic data for K-richterite were obtained using both *in-situ* and isotope dilution techniques. The *in-situ* analyses yielded initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of between 0.70600 and 0.70693 (n=12; Table 3), which overlap with the celestine values. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio obtained by isotope dilution is, after correcting for celestine contamination, ~ 0.7063 (Appendix in Supplementary Material), within the range of the *in situ* $^{87}\text{Sr}/^{86}\text{Sr}$ values measured.

3.5. S isotopes

Celestine from xenolith XM1/498 is characterised by a slightly heavy ^{34}S composition ($\delta^{34}\text{S} = 5.9\text{‰}$) compared to mantle values (e.g. MORB source $\delta^{34}\text{S} = -0.9 \pm 0.5\text{‰}$; Labidi et al., 2013). The $\delta^{34}\text{S}$ of celestine is higher than peridotitic sulphides included in diamonds (Eldridge et al., 1991; Rudnick et al., 1993) as well as sulphides in kimberlites and sulphide inclusions in kimberlite megacrysts (Chaussidon et al., 1989). However, the celestine values are similar to those of metasomatised peridotite xenoliths sampled by alkali basalts from the sub-continental lithospheric mantle (Ionov et al., 1992; Kyser, 1990) and of mantle wedge lavas (de Hoog et al., 1992; Fig. 7). The sulphur isotopes of celestine ($\Delta^{33}\text{S} = -0.01\text{‰}$; $\Delta^{36}\text{S} = -0.07\text{‰}$) are also within error of the ^{33}S - ^{34}S - ^{36}S mass-dependent fractionation trend defined by sedimentary rocks formed on the Earth after ~2.45 Gyr (Farquhar and Wing, 2003).

4. Discussion

4.1. Sulphate metasomatism of the MARID rock

Large grains of diopside appear to be absent from the primary MARID assemblage of xenolith XM1/498, which is consistent with observations from other MARID rocks (Dawson and Smith, 1977; Waters, 1987). The clinopyroxene grains that are typical of MARID rocks have compositions that are quite distinct from the diopside present in the sulphate veins (Figs. 3c and 4c). The sulphate veins also host a different mineral assemblage to the main MARID component of xenolith XM1/498 (i.e. K-richterite, phlogopite, ilmenite and rutile). This indicates that metasomatic fluid(s) permeated the rock at some stage after MARID formation, resulting in formation of the sulphate-rich veins.

Constraints on the composition of the metasomatic fluid are provided by the vein mineralogy. As celestine is the dominant phase in the veins, it is likely that the metasomatic fluid was unusually enriched in SO_3 . The occurrence of isolated inclusions and veinlets of celestine enclosed in euhedral clinopyroxene grains, which are, in turn, embedded by celestine, indicates co-precipitation of these phases. Other minerals observed in the sulphate-rich veins are phlogopite, pectolite, sphene and apatite (the latter enriched in F, S, Na, Sr and LREE), plus trace amounts of barite, calcite and emmonite. This mineral assemblage suggests crystallisation from a sulphate-rich fluid that was enriched in the alkali elements (Sr, Ba, Ca, Na and perhaps K), P, Ti and LREE, with lesser amounts of CO_2 , F and Si. However, dissolution of pre-existing K-richterite in the celestine veins and overgrowth of K-richterite by clinopyroxene indicates that some elements (e.g. Si, Ca, Na, K, Sr) could

have been provided by dissolution and/or replacement of MARID host minerals. The similar Sr/Ba ratios (Table 2 and Fig. 5) and identical Sr isotopes of celestine and K-richterite (Table 3 and Fig. 6) support the role of K-richterite as an important source of alkalis to the metasomatic fluid.

However, the celestine in xenolith XM1/498 contains significantly higher Sr concentrations ($\sim 4.3 \times 10^5$ ppm) than associated, partially replaced K-richterite (~ 700 ppm; Tables 1, 2). Therefore, the volume of replaced K-richterite in xenolith XM1/498 is clearly insufficient to account for the observed amount celestine. Consequently, the sulphate fluid must have contained significant quantities of dissolved Sr and alkalis, before reacting with the K-richterite. The formation of clinopyroxene at the expense of K-richterite (Fig. 2b, d) suggests that the sulphate fluid reacted with K-richterite to produce clinopyroxene, thus fractionating Ca from Sr and evolving towards more Sr-rich compositions.

As noted above, the composition of phlogopite in xenolith XM1/498 is uniform, irrespective of textural setting (i.e. coarse grains in the MARID matrix, small grains in the sulphate-rich veins). Phlogopite is partially replaced by pectolite, with pectolite also present along phlogopite cleavage planes (Fig. 2c; Fig. 2EA in Supplementary Material). These observations suggest that phlogopite in the sulphate-rich pools predates the metasomatic event. The euhedral habit of fine-grained phlogopite in the sulphate veins might indicate re-crystallisation of phlogopite upon interaction with the sulphate-rich fluid. Therefore, the presence of phlogopite in the sulphate-rich veins may not indicate a high K content in the sulphate-rich fluid.

The homogeneous composition of phlogopite contrasts with the large chemical variations of celestine, clinopyroxene and sphene. Celestine displays alternating bands with different Ba contents (Fig. 2e). Similar rhythmic banding in celestine has been

observed in large (~ 10 cm) celestine blades crystallised during diagenesis in sedimentary basins (Roedder, 1969) and in celestine grains formed during hydrothermal alteration of granites at relatively high temperature (~ 400°C; Hattori, 1989). These variations might indicate crystallisation from an infiltrating fluid that is periodically replenished, causing variation in Ba-Sr concentrations (i.e., multiple pulses of sulphate-rich fluid). The large chemical variations of the metasomatic phases in the sulphate-rich veins, and the possibility that these veins reflect multiple fluid pulses, complicates efforts to quantitatively resolve the chemical composition and pressure-temperature regime of the metasomatic fluids (see Table 5EA in Supplementary Material). The lack of inter- and intra-grain equilibrium implies that the sulphate metasomatic event occurred immediately before or during xenolith entrainment by the kimberlite magma.

In summary, the petrographic and mineral chemistry data are consistent with derivation of the sulphate-rich assemblage from interaction between an alkali-rich sulphate fluid and the MARID host rock. The sulphate fluid could be a melt or a brine (i.e., a saline hydrous fluid); in this regard, experiments on high temperature, high pressure brines have been shown that these brines are able to transport large amounts of dissolved sulphate (Newton and Manning, 2005), as well as other anions (e.g., P – Antignano and Manning, 2008) and cations that are largely immobile in hydrous fluids (e.g., Ti – Rapp et al., 2010). Sulphate vein formation probably occurred shortly before or during emplacement of the kimberlite magma. The main issue to address is whether the sulphate fluid permeated the MARID rock during mantle residence or after transportation into the upper crust.

4.2. Evidence for a mantle-derived sulphate fluid(s)

470

471 Sulphate minerals are far more common in crustal sedimentary and
472 hydrothermal environments than in magmatic systems and mantle rocks. The
473 concomitant enrichment in alkalis and SO_3 argues against a crustal origin for the fluid,
474 because the solubility of sulphate minerals in hydrous fluids under crustal conditions
475 (i.e., at low pressure) is extremely low (Newton and Manning, 2005 and references
476 therein). The replacement of celestine by serpentine (Figs. 2f, g, h) indicates
477 percolation of crustal hydrous fluids after sulphate vein formation. It is likely that this
478 alteration event occurred at relatively low temperatures, because celestine is
479 characterised by retrograde solubility (Hanor, 2000; Roedder, 1969), i.e. increasing
480 solubility with decreasing temperature. Low-T ($< 400^\circ\text{C}$) weathering is a common
481 feature of kimberlites and entrained xenoliths and is attributed to post-emplacement
482 percolation of hydrous fluids that are enriched in Si and Mg (Buse et al., 2010; Stripp
483 et al., 2006).

484 The Sr and S isotopic compositions of celestine support a mantle source for
485 the sulphate-rich fluids. The Sr isotopes of celestine fall within the range typical of
486 metasomatic rocks (and their mineral constituents) from the lithospheric mantle
487 beneath the Kaapvaal craton, including MARIDs and phlogopite–K-richterite
488 peridotites. Therefore, these data support a mantle origin for the sulphate fluid. The Sr
489 isotopic composition of celestine is significantly more radiogenic than that of Group I
490 kimberlites (Fig. 6), which rules out the entraining kimberlite magma as the main
491 source of Sr to the sulphate fluid. However, mixing between kimberlite fluids and
492 crustal components (e.g., assimilation of crustal xenoliths by kimberlite fluids or
493 interaction between kimberlite and crustal fluids) could produce the Sr isotopic
494 composition of the sulphate fluid (Fig 6).

495 The Kimberley kimberlites are emplaced into sedimentary and basaltic rocks
496 of the Karoo Supergroup (~300-180 Ma). The main country rocks are continental
497 lithic-rich sandstones, mudrocks and shales of the Eccra and Beaufort Groups, whereas
498 xenoliths of marine sandstones from the lower Eccra and Dwyka Groups are rare
499 (Hanson et al., 2009; Johnson et al., 1996). The Kimberley kimberlites also host
500 abundant xenoliths from the Archean (~2.7 Ga) Ventersdorp Supergroup (Hanson et
501 al., 2009), which display highly radiogenic Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}_{84\text{Ma}} > 0.713$; Fig. 6 –
502 Armstrong, 1987; Crow and Condie, 1988; Walraven et al., 1990; Whitelaw et al.,
503 2005). Therefore, interaction between kimberlite fluids and the Ventersdorp rocks
504 could have produced a fluid with Sr isotopes compatible with the sulphate fluid.

505 Further insights into possible fluid sources are provided by the S isotopes. If
506 the sulphate-rich veins in xenolith XM1/498 formed after kimberlite emplacement in
507 the crust, the metasomatic fluid could acquire S from three possible sources: i) the
508 Karoo sedimentary wall rocks; ii) the Ventersdorp xenoliths; or iii) residual kimberlite
509 fluids. Because there is negligible isotopic fractionation between (sulphate) fluids and
510 crystallised sulphates (Marini et al., 2011; Seal et al., 2000), the $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values
511 of celestine should be representative of the sulphate fluid.

512 Karoo sedimentary rocks of continental origin (e.g., from the Beaufort Group
513 – Catuneanu et al., 2005; Johnson et al., 1996) have $\delta^{34}\text{S}$ values that vary widely
514 depending on location within the basin (Bui et al., 2012; Maruoka et al., 2003).
515 Samples from the Permian-Triassic boundary in the northern Karoo basin, ~300 km
516 from Kimberley, show $\delta^{34}\text{S}$ values ranging mainly between -1 and +4‰ (Maruoka et
517 al., 2003). Importantly, most sulphur in these rocks is organically bound (Maruoka et
518 al., 2003), which makes it hard to mobilise by hydrothermal fluids. As oxidation of
519 sulphide minerals is a primary source of sulphate in basinal brines, another possible

source of sulphur might be the deep-marine rocks of the Dwyka and Eccu Groups. These sediments were deposited from the latest Carboniferous to the middle Permian (Catuneanu et al., 2005; Johnson et al., 1996), a period when there was a profound minimum in the sedimentary sulphides $\delta^{34}\text{S}$ record ($\delta^{34}\text{S} < 0\text{‰}$; Canfield and Farquhar, 2009). Therefore it is unlikely that the Karoo sedimentary rocks could have been the source of sulphur to the XM1/498 sulphate veins.

$\Delta^{33}\text{S}$ values provide a useful tool for tracing fluid interaction with Archean rocks (Bekker et al., 2009; Cabral et al., 2013; Fiorentini et al., 2012a, b; Penniston-Dorland et al., 2012), because $\Delta^{33}\text{S}$ only deviates significantly from zero in rocks older than ~ 2.45 Gyr (Farquhar and Wing, 2003; Farquhar et al., 2007; Philippot et al., 2012). As the $\Delta^{33}\text{S}$ value of XM1/498 celestine is close to zero (-0.01‰), this suggests negligible involvement of Archean Ventersdorp rocks in the genesis of the sulphate fluid(s).

The study of secondary fluid inclusions in kimberlite olivine has shown that kimberlite fluids can become progressively enriched in SO_3 during crystallisation (e.g., Golovin et al., 2007; Kamenetsky V. et al., 2007, 2009; Mernagh et al., 2011). The S isotopic composition of residual kimberlite fluids is difficult to estimate because a number of interplaying factors (e.g., oxygen fugacity, outgassing, fractional crystallisation, wall rock and xenolith assimilation) can contribute to fractionate the S isotopes to a different extent. Unfortunately, only limited S isotopic data are available for kimberlites. Muramatsu (1983) reported a $\delta^{34}\text{S}$ range of $-3.0 - +9.6\text{‰}$ for five bulk rock samples of South-African kimberlites. However, the selected samples included volcanic breccias, altered surface rocks and anomalously S-rich samples, which suggests that the values reported are not representative of primary kimberlite melts. Chaussidon et al. (1989) reported a single *in-situ* analysis of a sulphide grain from the

Bultfontein kimberlite ($\delta^{34}\text{S} = -0.1\text{‰}$), while S isotope analyses of sulphides and sulphates in 3 fresh kimberlite samples from the Udachnaya-East kimberlite (Yakutia, Russia) show $\delta^{34}\text{S}$ values of $+1 - +2\text{‰}$ and $\sim +14\text{‰}$, respectively (Fig. 7; Kamenetsky M., 2005). It is evident that the S isotopic composition of XM1/498 celestine ($\delta^{34}\text{S} = 5.9\text{‰}$) differs from that of the Udachnaya-East kimberlite sulphates, i.e. from the only kimberlitic sulphates analysed previously (Fig. 7). In addition, hydrothermal aqueous solutions, such as those occurring in kimberlite pipes after emplacement (Buse et al., 2010; Stripp et al., 2006), usually crystallise sulphates with $\delta^{34}\text{S}$ values between $+13$ and $+23\text{‰}$ (Marini et al., 2011), i.e. much higher than the celestine isotopes (Fig. 7). Although the above discussion does not definitively rule out the involvement of kimberlite fluids in the genesis of the celestine-rich veins, the S isotopic composition of celestine is considered poorly compatible with sulphur derivation from a residual kimberlite fluid.

From the above discussion, it is unlikely that the sulphate component of the metasomatic fluid was sourced from the crust or from residual kimberlite fluids, or from mixing between crustal and kimberlite components (e.g., contribution by Ventersdorp xenoliths would still provide S with $\Delta^{33}\text{S} \neq 0$, whereas $\Delta^{33}\text{S}_{\text{celestine}} \sim 0\text{‰}$). Therefore, the S isotopic evidence supports a mantle origin for the sulphate fluid.

If sulphate metasomatism occurred in the mantle, the $\delta^{34}\text{S}$ of celestine can be interpreted in terms of buffering of the sulphate fluid S isotopes by the sulphide component of the sub-continental lithospheric mantle. If equilibrium between the sulphate fluid ($\delta^{34}\text{S} = +5.9\text{‰}$) and SCLM mantle sulphides ($\delta^{34}\text{S} \sim +2\text{‰}$; Ionov et al., 1992) was achieved, then calculated equilibration temperatures vary between ~ 1050 and 1150°C (Miyoshi et al., 1984; Ohmoto and Rye, 1979 – Table 2EA). These

values might be close to the temperature of the sulphate fluid when it infiltrated the MARID rock.

4.3. Origin of the sulphate fluid

Low-degree partial melting of mantle rocks produces low-Si melts enriched in CO₂, H₂O, Cl, S and the other volatile species (Brey et al., 2008; Safonov et al., 2011; Wallace and Green, 1988). Experiments on S-rich basaltic compositions have shown that immiscible sulphate and sulphate-carbonate melts can separate from the original silicate melt (Jugo et al., 2005; Martin et al., 2012). There is also some evidence for the occurrence of immiscible sulphate melts in alkali-rich carbonate and silicate melts intruded into the crust (Naumov et al., 2008; Panina and Motorina, 2008 and references therein). Alkali-carbonate melts preserved in mantle rocks are enriched in sulphates (Giuliani et al., 2012). Therefore, we speculate that the sulphate fluid that produced the celestine-rich veins in xenolith XM1/498 formed by unmixing from a parental sulphate-rich alkali-carbonate (or silicate-carbonate) melt.

A second possible explanation is that the sulphate fluid(s) was produced by melting of a mantle source that was enriched in S and alkalis through incorporation of subducted components such as altered oceanic lithosphere and/or sulphate-rich marine sediments. For example, subduction of serpentinites has been shown to efficiently recycle S with $\delta^{34}\text{S} > +1 - +2\text{‰}$ into the mantle at depths beyond the formation of arc magmas (Alt et al., 2012). Under this scenario, the $\Delta^{33}\text{S}$ (~0) of celestine requires that the subducted component was younger than ~ 2.45 Ga (Jamieson et al., 2006). After Archean consolidation, the Kaapvaal craton experienced multiple accretionary events, the most significant being the Eburnian (~2.0-1.7 Ga), Kibaran (~1.2-1.0 Ga) and

Pan-African (~0.5 Ga; Thomas et al., 1993). During these events subduction occurred along the margins of the craton, which, could have introduced recycled material of crustal origin into the lithospheric roots of the craton. The large range of $\delta^{34}\text{S}$ values (-11 to +14‰) observed in eclogitic sulphides included in diamonds from the Kaapvaal craton (Fig. 7), is compelling evidence for the recycling of crustal S into the mantle beneath the Kaapvaal craton (Eldridge et al., 1991). The recycling of sulphur into the sub-continental lithospheric mantle has also been suggested by Ionov et al. (1992) and Wilson et al. (1996) who attributed $\delta^{34}\text{S}$ values of +5.0 – +7.5‰, measured in bulk xenoliths entrained by alkali basalt magmas, to metasomatism by slab-derived fluids.

Finally, a third possibility is that the alkali-rich sulphate fluid was residual after crystallisation of the main MARID minerals. This hypothesis is appealing because it would readily explain the similar Sr isotopic compositions of celestine and K-richterite in xenolith XM1/498 (Table 3 and Fig. 6). This interpretation might be supported by U-Pb ages (80-90 Ma) of zircon grains from another off-cut of xenolith XM1/498 (Konzett et al., 1998). These zircon ages indicate that MARID metasomatism slightly predated entrainment by the kimberlite magma (84 Ma; Allsopp and Barrett, 1975; Kramers et al., 1983), similarly to the timing inferred for the sulphate metasomatism.

5. Conclusions

In this study we have documented the occurrence of sulphate-dominated fluids in the Earth's mantle. MARID xenolith XM1/498, from the Bultfontein kimberlite, hosts an unusual vein assemblage of celestine, clinopyroxene and minor phlogopite,

pectolite, sphene, apatite, barite and Ca-Sr carbonates. The assemblage was likely produced by interaction between a sulphate fluid enriched in Sr, Ba, Ca, Na, P, Ti and LREE and minerals of the host MARID rock. Solubility data on sulphates in crustal hydrous fluids, Sr and S isotopic compositions of the vein minerals, and alteration of celestine by late-stage hydrous fluids rule out the possibility that the sulphate fluid(s) was of crustal origin. These data are consistent with the fluid(s) having a mantle origin, and with the metasomatism occurring at mantle depth, shortly before xenolith entrainment by the kimberlite magma. The sulphate fluid could have been produced by liquid immiscibility from a parental sulphate-rich alkali-carbonate melt, by partial melting of a mantle source that incorporated post-Archean subducted lithologies recycled into the mantle, or from residual fluids generated after crystallisation of the MARID assemblage.

Acknowledgments

We thank Alan Greig for assistance with the LA-ICP-MS analyses, Bence Paul for explaining the intricacies of the IOLITE software, and Graham Hutchinson for support with the SEM imaging and EMP analyses at the University of Melbourne. We are also grateful to Karsten Goemann for assistance with FE-SEM work at the Central Science Laboratory, University of Tasmania. This manuscript has benefitted from discussions with a number of colleagues including Roberta Rudnick, Andrew Tomkins and Roger Mitchell. Insightful reviews of Sonja Aulbach and an anonymous reviewer, and editorial handling of Bernard Marty have greatly improved the

643 manuscript. AG's PhD research is supported by an International Australian
644 Postgraduate Award.

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916

Figure captions

Figure 1. Photograph of an off-cut of xenolith sample XM1/498. The off-cut was cut across a layer dominated by K-richterite (kric) with minor phlogopite (phl); the layer is pervasively cross-cut by creamy-coloured sulphate-rich veins (sulf).

Figure 2. (a-f) SEM back-scattered electron (BSE) and (g, h) FE-SEM secondary electron (SE) images of the sulphate-rich veins and pools in xenolith XM1/498. In (a) note the pervasive sulphate veining of a layer dominated by K-richterite (kric; cf. Fig. 1). (b) Euhedral grains of clinopyroxene (cpx) with inclusions of K-richterite, and K-richterite remnants in a sulphate-rich vein. (c) Sulphate-rich pool with abundant celestine (cel), euhedral grains of clinopyroxene and phlogopite (phl), and aggregates of alternating grains of phlogopite and pectolite (pect). (d) Embayed contacts between celestine and K-richterite (highlighted by red arrows) due to partial resorption of K-richterite by the sulphate-rich fluid; this contrasts with the euhedral habit displayed by clinopyroxene in the sulphate-rich vein. Also note the inclusions of apatite (ap) in clinopyroxene. (e) Compositional banding in celestine, due to variable Ba concentrations (lighter-coloured bands are richer in Ba than darker bands). (f) Replacement of celestine by a Mg-Fe silicate phase (probably serpentine; srp) along grain edges and cleavage planes. (g, h) Partially altered celestine displaying porous texture; in (h), $\times 9000$ magnification reveals that the pores are occupied by serpentine.

Figure 3. Major oxide co-variation diagrams showing the compositional variations of (a) celestine, and (b, c) clinopyroxene in sulphate-rich veins of xenolith XM1/498. In (b) the clinopyroxene analyses show a trend of increasing Na_2O and decreasing MgO ,

away from the composition of K-richterite; this indicates that the compositional variations in clinopyroxene are not due to inheritance from replaced K-richterite or to diffusion from adjacent K-richterite. In (c) note the different composition of vein clinopyroxene with respect to diopside in other MARID rocks (MARID Cpx; data on MARID minerals from Waters, 1987).

Figure 4. Compositional fields showing the range of primitive mantle (PM)-normalised trace element abundances for XM1/498 K-richterite (a), phlogopite (b) and vein clinopyroxene (c). Compositional fields of MARID minerals from Grégoire et al. (2002); PM composition from McDonough and Sun (1995).

Figure 5. Plots showing (a) log Sr/Ca (by weight) vs log Sr/Ba (by weight), and (b) log Sr/Ca (by weight) vs log Ba/Ca (by weight) for celestine and clinopyroxene from the sulphate-rich veins in xenolith XM1/498, as well as K-richterite and phlogopite.

Figure 6. Comparison between $^{87}\text{Sr}/^{86}\text{Sr}$ values (at 84 Myr, the emplacement age of the Bultfontein kimberlite – Allsopp and Barrett, 1975; Kramers et al., 1983) of XM1/498 celestine, K-richterite and other mantle lithologies. The asterisk indicates that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of kimberlites are initial values. The Ventersdorp volcanic rocks include mafic lavas (Armstrong, 1987; Crow and Condie, 1988), hydrothermally altered lavas (Whitelaw et al., 2005) and quartz porphyries (Walraven et al., 1990). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of South African Group I and II kimberlites are from Woodhead et al. (2009). The MARID and phlogopite–K-richterite peridotites include bulk rock (Hawkesworth et al., 1990) and mineral separate analyses (Kramers et al., 1983).

967

968 **Figure 7.** Comparison between $\delta^{34}\text{S}$ values of XM1/498 celestine and other mantle
969 and crustal rocks/minerals. ‘Northern Karoo sediments’ include analyses of
970 sedimentary rocks of continental origin from the Permian-Triassic boundary (Beaufort
971 Group) in the northern Karoo basin, ~300km from Kimberley (Maruoka et al., 2003).
972 ‘Kimberlite sulphides’ include a single analysis of a pyrrhotite grain from the
973 Bultfontein kimberlite (Chaussidon et al., 1989) and analyses of sulphides from the
974 Udachnaya-East kimberlite (Yakutia, Russia; Kamenetksy M., 2005). ‘Kimberlite
975 sulphates’ indicate analyses of sulphates from the same Udachnaya-East samples. The
976 $\delta^{34}\text{S}$ range of the ‘continental lithospheric mantle’ includes bulk rock analyses of 90
977 peridotite and pyroxenite xenoliths sampled by alkali-basalts in Siberia and Mongolia
978 (Ionov et al., 1992) and 6 garnet peridotite xenoliths from South-African kimberlites
979 (Kyser, 1990). Other data sources: sulphides in kimberlite megacrysts (Chaussidon et
980 al., 1989); sulphide inclusions in diamonds (Eldridge et al., 1991; Rudnick et al.,
981 1993; Thomassot et al., 2009); MORB glasses (Labidi et al., 2012); mantle wedge
982 lavas (de Hoog et al., 2001); hydrothermal sulphates (Marini et al., 2011).

Highlights

- An unusual sulphate-rich vein assemblage in a mantle MARID xenolith
- The assemblage is dominated by celestine (SrSO_4) and includes silicates, apatite and carbonates
- This paragenesis is attributed to an alkali-rich sulphate fluid
- Sr and S isotopes and geochemical arguments constrain a mantle origin
- First ever reported evidence for a sulphate-dominated fluid in the mantle

Figure 1
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Figure 2
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Figure 5

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Figure 6

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Figure 7
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Table 1
Major oxide composition (wt.%) of minerals in xenolith XM1/498

	K-richterite		phlogopite		celestine	clinopyroxene	sphene	pectolite
	average ^a	1σ	average ^b	1σ	variation ^c	variation	variation	498-pect 1
SiO ₂	55.02	0.57	41.51	0.49		52.61 – 54.16	29.16 – 30.59	52.95
TiO ₂	0.51	0.14	1.09	0.08		0.53 – 1.17	30.83 – 37.44	bdl
Al ₂ O ₃	0.74	0.06	10.46	0.16	≤ 0.10	0.04 – 0.76	0.04 – 0.10	0.03
Cr ₂ O ₃	0.21	0.04	0.13	0.03	≤ 0.05	0.17 – 0.59	≤ 0.02	bdl
FeO	4.50	0.11	7.36	0.13	≤ 0.13	3.47 – 6.10	2.02 – 6.85	0.37
MnO	0.06	0.01	0.04	0.03	≤ 0.02	0.06 – 0.24	≤ 0.05	0.09
MgO	20.91	0.28	23.43	0.38	≤ 0.01	16.00 – 19.26	0.03 – 0.34	0.02
NiO	0.05	0.02	0.15	0.03	≤ 0.06	≤ 0.09	≤ 0.05	0.01
SrO	0.05	0.02	0.03	0.01	40.16 – 56.24	≤ 0.10	≤ 0.12	bdl
BaO	0.02	0.02	0.06	0.03	0.03 – 17.72			bdl
CaO	6.37	0.17	0.02	0.04	0.04 – 0.51	19.14 – 23.21	27.10 – 28.54	33.64
Na ₂ O	4.09	0.08	0.13	0.05	≤ 0.05	0.53 – 1.71	≤ 0.12	8.49
K ₂ O	4.91	0.16	10.29	0.23	0.01 – 0.08	≤ 0.04	≤ 0.16	0.08
ZrO ₂							0.06 – 0.22	
V ₂ O ₃							0.11 – 0.24	
Nb ₂ O ₅							0.38 – 0.62	
SO ₃					39.90 – 44.39			
Cl	0.01	0.00	0.02	0.00				0.01
Total	97.46	0.72	94.73	0.95	97.33–101.23	98.76–100.73	95.14 – 97.70	95.68
O=Cl	0.00	0.00	0.01	0.00				0.00
H ₂ O calc			3.92	0.05				
Total calc	97.46	0.72	98.65	1.00				95.68
Mg#	89.2	1.3	85.0	0.3		83.3 – 90.0		

^a 11 analyses; ^b 10 analyses; ^c 25 analyses; ^d 16 analyses; ^e 8 analyses
Mg# = 100×Mg/(Mg+Fe²⁺); bdl below detection limit
phosphorus below detection limit in K-richterite, phlogopite, celestine and clinopyroxene
full data-set in Supplementary Material, Table 3EA

Table 2

Trace element composition (ppm) of minerals in xenolith XM1/498

	K-richterite		phlogopite		celestine	clinopyroxene	pectolite
	average ^a	1σ	average ^b	1σ	variation ^c	variation ^d	498-pect 1
Rb	31.0	1.6	541	19	0.02 – 0.17	≤ 6.07	1.9
Ba	33.8	11.8	492	54	9148 – 119799	0.3 – 66.5	18
Th	0.32	0.29	2.9	0.8	bdl	0.03 – 0.30	0.03
U	0.08	0.09	0.26	0.10	bdl	≤ 0.07	0.15
Ta	0.13	0.06	0.21	0.07	bdl	≤ 0.19	nd
Nb	4.2	1.4	7.1	0.9	bdl	0.09 – 1.64	0.03
La	4.3	2.4	0.08	0.08	0.03 – 0.39	5.9 – 34.9	0.33
Ce	10.2	4.6	0.23	0.23	≤ 0.01	27 – 130	0.11
Pb	5.7	0.8	0.20	0.17	≤ 0.07	0.25 – 1.25	0.07
Pr	nd		0.02	0.02	bdl	5.5 – 20.5	nd
Sr	684	25	17.6	8.9	int std	273 – 968	477
Nd	4.5	1.6	0.07	0.06	≤ 0.01	29 – 107	bdl
Zr	28.1	4.9	1.22	0.62	≤ 0.03	39 – 135	0.02
Hf	1.35	0.18	0.04	0.03	bdl	1.9 – 5.0	nd
Sm	0.61	0.24	0.01	0.02	0.03 – 0.18	7.7 – 21.4	bdl
Eu	0.16	0.05	0.01	0.01	0.11 – 1.31	2.0 – 5.6	0.03
Ti	2847	280	6117	619	23 – 43	2036 – 5672	29
Gd	0.29	0.11	0.01	0.02	≤ 0.03	5.5 – 13.9	nd
Dy	0.13	0.05	bdl		bdl	2.8 – 6.2	bdl
Ho	nd		bdl		bdl	0.41 – 0.70	nd
Er	0.04	0.02	0.01	0.01	bdl	0.76 – 1.54	0.02
Yb	0.04	0.02	0.01	0.02	bdl	0.30 – 0.82	0.06
Y	0.45	0.18	0.02	0.02	0.7 – 3.3	8.6 – 19.4	0.01
Lu	0.01	0.00	bdl		bdl	0.02 – 0.09	nd
V	253	7	90	5	0.09 – 0.12	330 – 409	1.2
Sc	39.1	0.8	4.5	0.2	≤ 0.02	47 – 61	6.1
Li	1.8	0.4	7.6	0.8	≤ 0.03	1.09 – 1.97	0.09
Ni	475	16	1139	39	0.03 – 0.04	338 – 411	3.8
Ca	int std		139	59	nd	int std	nd
Sr/Ca ^e	0.015	0.001	0.13	0.06	126 – 1080	0.002 – 0.006	
Sr/Ba ^e	20.8	7.9	0.04	0.02	2 – 153	15 – 1501	
Ba/Ca ^e	0.0008	0.0004	3.7	0.8	1 – 505	1.9×10 ⁻⁶ – 4.3×10 ⁻⁴	

^a 9 analyses; ^b 11 analyses; ^c 6 analyses; ^d 10 analyses^e Ca from electron microprobe analyses, excepted phlogopite (ICP-MS); Sr and Ba from ICP-MS analyses, excepted celestine (EMP)

bdl below detection limit; nd not determined; int std internal standard

full data-set in Supplementary Material, Table 4EA

Table 3

Solution and in-situ analyses of the Rb-Sr isotopes of celestine and K-richterite in xenolith XM1/498

	Rb ppm ^a	Sr ppm ^a	⁸⁷ Rb- ⁸⁷ Sr isobaric interference (%)	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr _i ^c
				2σ ^b	2σ ^b	
<i>Solution analyses</i>						
498 K-richterite 1	29.1	2166		0.0388	0.0002	0.706546
498 K-richterite 2	29.0	1623		0.0517	0.0002	0.706760
<i>In-situ analyses</i>						
K-richterite 1			28.0	0.2748	0.0012	0.70680
K-richterite 2			28.5	0.2821	0.0012	0.70679
K-richterite 3			27.9	0.2734	0.0013	0.70633
K-richterite 4			29.5	0.2955	0.0013	0.70709
K-richterite 5			28.5	0.2816	0.0016	0.70693
K-richterite 6			27.4	0.2665	0.0016	0.70723
K-richterite 7			26.8	0.2583	0.0012	0.70635
K-richterite 8			28.2	0.2775	0.0021	0.70716
K-richterite 9			27.3	0.2649	0.0010	0.70662
K-richterite 10			26.6	0.2555	0.0012	0.70688
K-richterite 11			26.9	0.2604	0.0024	0.70724
K-richterite 12			28.3	0.2792	0.0010	0.70666
celestine 1			0.0	0.00012	0.00003	0.70672
celestine 2			0.0	0.00009	0.00003	0.70686
celestine 3			0.0	0.00009	0.00002	0.70684
celestine 4			0.0	0.00007	0.00003	0.70683
celestine 5			0.0	0.00007	0.00003	0.70678
celestine 6			0.0	0.00005	0.00002	0.70673
celestine 7			0.0	0.00005	0.00003	0.70691
celestine 8			0.0	0.00003	0.00003	0.70675
celestine 9			0.0	0.00002	0.00003	0.70669

^a Trace element concentration based on ICPMS data for splits of the K-richterite solutions; the in-situ ICPMS analyses of K-richterite produced average Rb and Sr concentrations of 31.0±1.6 and 684±25 ppm (Table 2). The higher Sr contents displayed by the solution analyses are due to celestine contamination.

^b Within-run uncertainty

^c Initial ⁸⁷Sr/⁸⁶Sr at 84 Myr, which is the emplacement age of the Bultfontein kimberlite (Allsopp and Barrett, 1975; Kramers et al., 1983)

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