Tracing mantle metasomatism using combined stable (S, O, N) and radiogenic (Sr, Nd, Hf, Pb) isotope geochemistry: case studies from mantle xenoliths of the Kimberley kimberlites

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Introduction

Mantle fluids continuously (or intermittently) transfer chemical species across reservoirs, thus modifying the composition of different mantle domains. To improve understanding of mantle evolution, it is therefore important to establish criteria to constrain the origin and evolution of mantle fluids. The sub-cratonic lithospheric mantle is a long-lived (>3 Ga) reservoir, which has experienced multiple episodes of metasomatic enrichment. Metasomatised mantle xenoliths entrained by kimberlite magmas during ascent through craton interiors therefore provide ideal candidates to investigate mantle fluids.

Samples, methods and results

Here we document the results of a multi-isotope study of mantle xenoliths from the Boshof Road dumps, which host historical waste material from mining of the ~84 Ma Bultfontein Kimberlite (Kimberley, South Africa). The sample suite includes phlogopite-rich peridotites hosting clinopyroxene and/or LIMA (lindsleyite-mathiasite) titanates, wehrlites, MARID rocks and a mantle polymict breccia (Table 1). Five samples include variably fresh sulfide grains, whose S isotope ratios were measured by bulk-rock and *in situ* SIMS methods. The O isotope composition of mineral separates from each xenolith, plus two additional (modally) unmetasomatised peridotites (Table 1) were analysed using the laser fluorination technique. The N isotope systematics of phlogopite were examined using a seal-tube combustion technique combined with conventional static mass spectrometry. The Sr-Nd-Hf-Pb isotope composition of clinopyroxene, K-richterite and LIMA were measured using MC-ICPMS with a combination of *in situ* (Sr only) and solution-mode methods.

The oxygen isotope composition of olivine grains is remarkably consistent among the examined samples, including modally unmetasomatised samples, and overlaps with that of olivine in mantle peridotites worldwide ($\delta^{18}O$ = 5.18 ± 0.14, 1sd; Mattey et al., 1994). Conversely, the $\delta^{18}O$ values of clinopyroxene grains, a typical metasomatic phase in the sub-cratonic mantle, in the peridotite samples range to below typical mantle values (5.57 ± 0.18, 1sd; Mattey et al., 1994) (Fig. 1). The $\delta^{34}S$ values of sulfide grains in four peridotites and a polymict breccia vary between ~-1 and -6‰, with most values being between -2 and -5‰ (Fig. 1; Giuliani et al., 2016). Phlogopite $\delta^{15}N$ compositions are between +4.4 and +6.2‰ (five

peridotites, one MARID), which is significantly different from the mantle signature of -5 ± 2‰ inferred from studies of diamonds and oceanic basalts (e.g., Cartigny and Marty, 2013).

Table 1. Petrographic features, T, P and age constraints for studied mantle xenoliths

sample name	*lithology*	*equilibrium T (°C)*	*equilibrium P (GPa)*	*Age of metasomatism (Ma)*	*isotopic systems examined*
XM1/355	garnet harzburgite	1060-1100	4.7-4.9	no metasomatism	O
XM1/422	spinel harzburgite	680-710	2.7-2.8	no metasomatism	O
XM1/371	Phl-rich wehrlite	1120-1160	5.0-5.1	no constraints	O, S, N, Sr, Nd, Hf, Pb
BLFX-2	garnet wehrlite	1040-1080	4.2-4.4	no constraints	O, Sr, Nd, Hf, Pb
XM1/142	Phl-rich Spl harzburgite	750-860	3.0-3.5	82 ± 3[a]	O, S, N, Sr, Nd, Hf, Pb
XM1/341	LIMA-bearing Phl-rich Spl lherzolite	830-910	3.4-3.8	177 ± 12[b]	O, S, N, Sr, Nd, Hf, Pb
XM1/345	LIMA-bearing Phl-rich Spl harzburgite	750-850	3.0-3.4	178 ± 29[b]	O, S, N, Sr
XM1/362	LIMA-bearing Phl-rich Spl lherzolite	770-830	3.1-3.4	190 ± 24[b]	O, S, N, Sr, Nd, Hf, Pb
XM1/331	MARID	-	-	129.8 ± 2.0[c]	O, Sr, Nd, Hf, Pb
XM1/498	Cpx-free MARID	-	-	80-90[d]	O, N, Sr, Nd, Hf
BLFX-3	Cpx-free MARID	-	-	no constraints	O, Sr, Nd, Hf, Pb
DU-1	polymict breccia	850-900	3.4-3.7	~80-90[e]	S

[a] zircon U/Pb age (Konzett et al., 2000); [b] LIMA U/Pb age (Giuliani et al., 2014b); [c] maximum zircon U/Pb age (Giuliani et al., 2015); [d] zircon U/Pb age (Konzett et al., 1998); [e] metasomatism coeval with kimberlite magmatism in the Kimberley area (Giuliani et al., 2014a)

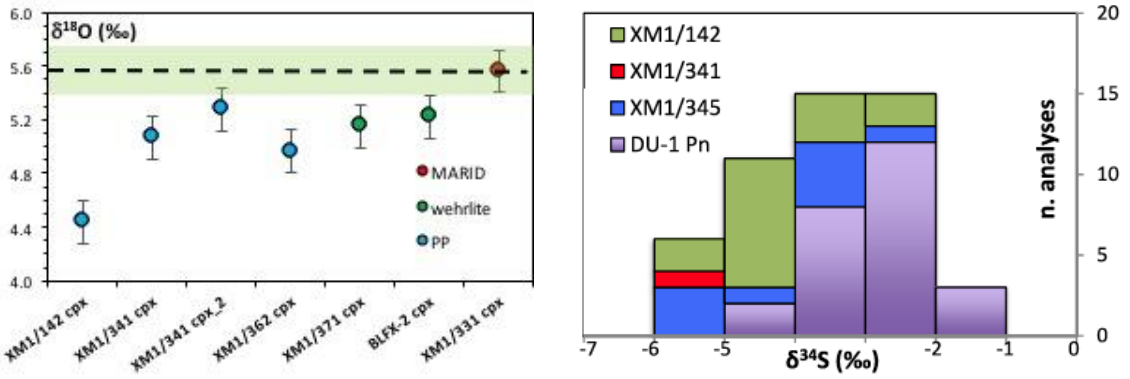

Figure 1. Left panel: Oxygen isotope composition of clinopyroxene grains; the green band represents the mantle range ($\delta^{18}O$ = 5.57 ± 0.18, 1sd; Mattey et al., 1994). Right panel: In-situ S isotope analyses of pentlandite (Pn) grains.

The Sr-Nd-Hf isotope composition of metasomatic phases vary considerably between xenolith types. Clinopyroxene in the two wehrlite samples exhibit similar values (εNd_{84Ma} = 3.2-3.7, εHf_{84Ma} = 2.0-2.1) in the range of southern African Cretaceous archetypal kimberlites. Metasomatic phases in the phlogopite-rich xenoliths, including two MARID samples, show a large compositional range from values (εNd_{84Ma} = -8 to -13, εHf_{84Ma} = -13 to -17) typical of metasomatised lithospheric mantle magmas (e.g., lamproites, orangeites) to compositions below the Nd-Hf mantle array (i.e. $\Delta\varepsilon Hf_{84Ma}$ = -10 to -12 and εNd_{84Ma} = -3 to -5), and similar to those of southern African transitional kimberlites.

LIMA minerals exhibit variable initial Sr isotope ratios ($^{87}Sr/^{86}Sr$ ~0.705 to ~0.713) at every scale (from between samples to within a single grain). In each sample, two or three generations of LIMA minerals can

be distinguished based on trace element and Sr isotope variations. However, U/Pb dating of LIMA grains indicates a single episode of LIMA formation at ~180-185 Ma for each xenolith (Giuliani et al., 2014b).

Discussion

The S isotope systematics are inconsistent with the metasomatic agent(s) that introduced sulfides into the Bultfontein mantle being sourced in the depleted asthenospheric mantle, whose $\delta^{34}S$ is ~ -1.4‰ (Labidi et al., 2013). $\delta^{34}S$ values as low as -6‰ require input from recycled crustal material, perhaps sulfide-bearing sediments. The interpretation that subducted material occurred in the source of the metasomatic fluids is strenghtened by the O and N isotope data for clinopyroxene and phlogopite, respectively. Furthermore, sulfide S and phlogopite N isotope compositions are remarkably homogeneous across the sample suite despite the variable style, P-T conditions and age of metasomatism (Table 1). This might indicate that metasomatic mantle fluids beneath Kimberley tapped a relatively homogeneous (sub-lithospheric?) source over a time-span extending from ~180 Ma (i.e. Karoo) to ~80-90 Ma (i.e. kimberlite emplacement age). This view is at odds with the diverse range of recorded Sr-Nd-Hf compositions, which instead suggest contributions from different sources including the asthenospheric (see the wehrlites) and lithospheric mantle (see some of the phlogopite-rich xenoliths). This apparent contradiction could be reconciled by accounting for the progressive evolution of the fluid(s) source with attendant radiogenic ingrowth; and if the Sr-Nd-Hf (and O) isotope compositions were affected by interaction with lithospheric wall rocks to a larger and more variable extent than the N-S isotope systems. The variable Sr isotope compositions of coeval LIMA grains might further highlight the fundamental contribution of lithospheric protoliths and/or wall rocks to the radiogenic isotope compositions of some metasomatic phases.

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