



Oxygen and hydrogen isotopic composition of phlogopites and amphiboles in diamond-bearing kimberlite hosted MARID xenoliths: Constraints on fluid-rock interaction and recycled crustal material in the deep continental lithospheric mantle

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ABSTRACT

MARID (Mica-Amphibole-Rutile-Ilmenite-Diopside) xenoliths are transported from the deep-cratonic lithosphere to the Earth's surface by Cretaceous kimberlites emplaced in the Kimberley area of the Kaapvaal Craton. MARID xenoliths have high modal abundances (70–80 vol%) of mica and amphibole, indicating their origin from a hydrous source. The $\delta^{18}\text{O}$ values ($4.7 \leq \delta^{18}\text{O} \leq 6.9\text{‰}$) of phlogopite micas from 14 MARID samples indicate that these minerals are both ^{18}O -enriched and ^{18}O -depleted with respect to the average upper mantle $\delta^{18}\text{O}$ value of $5.8 \pm 0.6\text{‰}$. The range of $\delta^2\text{H}$ values of phlogopites ($-83 \leq \delta^2\text{H} \leq -53\text{‰}$, $n = 14$) of MARID xenoliths are slightly larger than the average mantle $\delta^2\text{H}$ value ($-70 \pm 10\text{‰}$). The oxygen ($\Delta^{18}\text{O}_{\text{phlogopites-amphibole}} = -0.4$ and 0.4‰) and hydrogen ($\Delta^2\text{H}_{\text{phlogopite-amphibole}} = 14$ and 36‰) isotopic disequilibrium recorded from two MARID xenoliths suggests the duration of the last isotopic exchange, possibly just before the kimberlite emplacement, between these minerals and metasomatic fluids was too short to reach isotopic equilibrium. Our model calculation indicates that the phlogopites of MARID xenoliths underwent isotopic exchange with fluids of $\delta^{18}\text{O} = 5.5$ to 10‰ , $\delta^2\text{H} = -62$ to -90‰ . The range of $\delta^{18}\text{O}$ value of the calculated metasomatic fluids resembles the oxygen isotopic composition of the primary mantle carbonate ($\sim 6\text{--}9\text{‰}$) suggesting interaction between carbonatic melt and MARID xenoliths in the continental lithospheric mantle. Furthermore, $\delta^{18}\text{O}$ values of phlogopites together with previously published nitrogen isotope data ($-11 \leq \delta^{15}\text{N} \leq 9\text{‰}$; Banerjee et al., 2015) indicates incorporation of inhomogeneously distributed recycled crustal material from subducted crust within their source magma. Therefore, O-H-N isotope data for MARID xenoliths indicates their crystallization from geochemically heterogeneous magma in the upper continental mantle and subsequent metasomatism with mantle fluids.

1. Introduction

The oxygen and hydrogen isotopic composition of the mantle has been primarily investigated by the study of two major rock types; basalts and peridotite xenoliths (e.g. Bindeman, 2008; Bindeman et al., 2005; Chazot et al., 1997; Eiler, 2001; Eiler et al., 2000a; Eiler et al., 1998; Harmon and Hoefs, 1995; Kyser, 1986; Kyser and O'Neil, 1984; Kyser et al., 1981, 1982; Matthey et al., 1994a; Poreda et al., 1986; Shaw et al., 2008). The oxygen isotopic composition of the oceanic upper mantle sampled by mid-ocean ridge basalts (MORBs) has a uniform value of $5.7 \pm 0.2\text{‰}$ (Harmon and Hoefs, 1995; Kyser et al., 1982).

However, oxygen isotopic compositions of island arc basalts and their olivine phenocrysts record a wide range of values from 4.1 to 7.5‰ (Bindeman, 2008; Bindeman et al., 2005; Eiler et al., 1998; Eiler et al., 1996; Eiler et al., 1997; Eiler et al., 2000b; Kyser et al., 1982), suggesting contributions of subducted and crustal material into their source (Harmon and Hoefs, 1995; Bindeman et al., 2005). Similarly, oxygen isotopic compositions of continental basalts record a wide range of values from 4.8 to 11.4‰ (averaging $6.4 \pm 1.1\text{‰}$; Harmon and Hoefs, 1995) suggesting crustal contamination during their formation.

The major minerals, olivines and pyroxenes, in mantle peridotite xenoliths mostly exhibit identical ranges in oxygen isotopic

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composition (4.8 to 6.1‰), suggesting near oxygen isotopic equilibrium between these two minerals at mantle temperatures (Mattey et al., 1994a, 1994b; Chazot et al., 1997). However, a wider range of oxygen isotopic composition of olivines (~3‰) than coexisting pyroxenes (~1‰) was also reported from upper mantle peridotites (Kyser et al., 1981, 1982), and interpreted either as: different temperatures of isotopic equilibrium between these two minerals in the mantle (Kyser et al., 1981, 1982); or differences in the rate of isotope exchange between each of these minerals and metasomatizing mantle fluids (Gregory et al., 1986).

The oxygen isotopic composition of another important component, primary and secondary carbonates associated with kimberlites (1.2 to 26.6‰; Deines, 2002; Giuliani et al., 2014; Tappe et al., 2017) from the continental mantle, exhibit much wider range than that reported from olivines and pyroxenes of mantle peridotites. This wide range of $\delta^{18}\text{O}$ values were interpreted in two ways: (1) oxygen isotopic exchange in closed system condition between primary mantle carbonates ($\delta^{18}\text{O} \approx 6$ to 9‰; Demény et al., 1998; Giuliani et al., 2014) and $\text{CO}_2/\text{H}_2\text{O}$ fluid as a function of temperature (Wilson et al., 2007; Tappe et al., 2008; Tappe et al., 2017); or (2) interaction of primary carbonates with late-stage magmatic fluid, meteoric water, hydrothermal fluid, and incorporation of crustal material (Giuliani et al., 2014).

Hydrogen isotope ratios of MORBs vary from –81 to –33‰ indicating complex processes, such as outgassing, hydration, and mantle metasomatism associated with these rocks (Kyser and O'Neil, 1984; Poreda et al., 1986). Furthermore, hydrogen isotope ratios of melt inclusions from island arc basalts vary from –55 to –12‰ indicating incorporation of ^2H -rich fluids with respect to the mantle hydrogen isotopic composition (-70 ± 10 ‰; Kyser and O'Neil, 1984) from dehydrated subducted crust within their source magma (Shaw et al., 2008).

The incorporation of crustal or subducted material, metasomatism, and degassing are three major processes, which are principal factors for the variation of oxygen and hydrogen isotopic composition of the mantle. Kimberlites directly sample the deepest continental mantle, and kimberlite-hosted MARID xenoliths represent a part of this mantle. The crystallization temperature and pressure of MARID xenoliths ranges from 933 to 984 °C and 3.9 to 4.2 GPa (Konzett et al., 2014), respectively, also suggesting their formation in the deep continental mantle. Furthermore, the high modal abundance of amphibole and mica of 70–80 vol% indicates their formation from hydrous magma in the continental mantle, in contrast to olivine- and clinopyroxene-bearing mafic and ultramafic mantle rocks. This study investigates the processes in the deep continental lithospheric mantle responsible for the variation of oxygen and hydrogen isotopic compositions of mica and amphibole in MARID xenoliths.

2. Geological setting

The MARID xenoliths were hosted by kimberlite pipes emplaced in the Kimberley area, located at the south-western margin of the Kaapvaal Craton, South Africa (Fig. 1). The Archean Kaapvaal Craton at the south of the Limpopo mobile belt and the Zimbabwe Craton (Jacobs et al., 2008) was formed from the amalgamation of two major Archaean terranes - the Witwatersrand block and the Kimberley block along the Colesberg lineament between 2.88 and 2.93 Ga (Schmitz et al., 2004; Aulbach et al., 2009). The western edge of the Kaapvaal Craton is bounded by the Kheis Belt that was formed between 1.7 and 2.0 Ga during compression and eastward thrusting of the passive margin west of the Colesberg lineament (Cornell et al., 1998; Griffin et al., 2003; Jacobs et al., 2008). The southern edge of the Kaapvaal Craton is bounded by the Namaqua-Natal fold belt that was formed from arc accretion and continent collision between 1.05 and 1.1 Ga (Jacobs et al., 2008; Shirey et al., 2004).

Major kimberlite occurrences in the Kimberley area include Bultfontein, De Beers, Dutoitspan, Wessleton, and Kimberley pipes. The

MARID xenolith samples investigated in this study were collected from the Bultfontein Dumps located at Boshof Road, Kimberley.

The host lithologies of the Bultfontein kimberlite includes Karoo sedimentary rocks consisting of mainly shale of the Dwyka Formation, Karoo dolerite sills emplaced at 181–185 Ma (Jourdan et al., 2007; Svensen et al., 2012), andesitic-to-basaltic lavas intercalated with quartzite layers of the 2.7 Ga Ventersdorp Supergroup (Poujol et al., 2003) and felsic gneisses of the Archean basement. The Bultfontein kimberlite consists of a regular-shaped diatreme tapering into a dyke nearly 850–900 m below the present surface (Clement, 1982; Field et al., 2008; Giuliani et al., 2017). The Bultfontein kimberlite consists of a hypabyssal kimberlite that is an enlarged lower dyke, and a kimberlite breccia, surrounded by a volumetrically-dominant Kimberley-type pyroclastic kimberlite (Clement, 1982; Field et al., 2008).

The kimberlites of the Kimberley area were emplaced between 81 and 90 Ma (Allsopp and Barrett, 1975; Davis, 1977; Kramers et al., 1983; Batumike et al., 2008; Griffin et al., 2014) after lamproite (a.k.a orangeites) emplacement in the Barkly West-Boshof district between 115 and 128 Ma (Smith et al., 1985; Phillips et al., 1999; Giuliani et al., 2017; Tappe et al., 2018). A Rb/Sr age of 84.0 ± 0.9 Ma was obtained for the Bultfontein kimberlite from phlogopite in metasomatised mantle xenoliths (Kramers et al., 1983).

3. Methods

Polished thin-sections of MARID xenoliths were initially studied in transmitted and reflected light using a petrographic microscope. Mineral compositions were determined on 20 polished thin sections using a JEOL JXA-8230 electron microprobe at Queen's University, Canada. The analyses used an accelerating voltage of 15 kV, a beam current of 20 nA, a beam diameter of 5–10 μm , and counting time of 10s. Natural standards from the Smithsonian Institute were used for the analysis of all phases. The reported data represent an average of three or more analyses of each grain, and of at least three grains from different parts of each sample.

For stable isotope ratio analysis, samples were crushed, sieved, and then washed with distilled water. Amphiboles and micas were separated from the samples by hand-picking under a binocular microscope. Both oxygen and hydrogen isotope ratios were measured at the Queen's Facility for Isotope Research (QFIR) at Queen's University, Canada. Stable isotope ratios are reported in delta (δ) notation as parts per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW). The analytical precisions (2σ) for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are better than 0.2 and 3‰, respectively.

Oxygen was liberated from silicate samples by reaction with BrF_5 using the technique of Clayton and Mayeda (1963). The cryogenically collected CO_2 gases were analyzed for oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$) with a Thermo-Finnigan MAT 252 stable isotope ratio mass spectrometer. One certified international standard, NBS-28 (quartz, $\delta^{18}\text{O} = 9.6 \pm 0.1$ ‰), was analyzed along with 9 samples in each sequence (one sequence = 10 samples) to monitor QA/QC of $\delta^{18}\text{O}$ values of minerals. The hydrogen isotope ratios of samples were analyzed by a Thermo-Finnigan high temperature conversion elemental analyzer (TC/EA) in-line with a Thermo-Finnigan Delta plus XP isotope ratio mass spectrometer using a modified procedure from Sharp et al. (2001). Samples were weighed (~1 mg) into 5 mm \times 3.5 mm silver capsules and heated for 1 h at 100 °C in an oven. The silver capsules were compacted and placed into a zero-blank auto sampler. The compacted silver capsules were dropped from the auto sampler into a ceramic tube that contained a glassy carbon tube filled with glassy carbon chips for the reduction of samples at 1450 °C. The samples were converted to H_2 and CO from the reaction between released H_2O from samples and glassy carbon (C). Subsequently, the gases (H_2 and CO) were transferred with helium carrier gas via 1-meter molecular sieve 5A gas chromatography column into the mass spectrometer for measurement of the hydrogen isotopic composition and water content (wt%). One certified

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