

## Metasomatism of the deep root of the Slave craton by melts from subducted oceanic crust

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### Introduction

Mantle xenoliths geochemically record the mechanisms that form and modify the subcontinental lithospheric mantle (SCLM), such as decompression melting, subduction-related flux melting, metasomatism, and refertilization. These different processes distinctively alter the chemistry of mantle xenoliths before their eruption and allow for the identification of mantle processes that modify the SCLM.

Stable isotopes are a powerful tool for examining material fluxes between the Earth's surface and interior and thus provide a means of testing the sources of metasomatic fluids and whether recycled components are present in the SCLM. Stable isotope fractionation between mineral and melt phases at magmatic temperatures is small, thereby providing little leverage for either partial melting or fractional crystallization to significantly affect isotope compositions (e.g., Eiler, 2001). However, water-rock reactions at or near Earth's surface produce larger isotopic fractionations. Therefore, when surficial reservoirs (e.g., sediments, altered oceanic crust, serpentinites) are returned to the mantle via subduction, melts or fluids generated during the subduction process have the potential to interact with and change the isotopic composition of the overlying mantle wedge. In this study, we combine  $\delta^{18}\text{O}$ ,  $\delta^{44/40}\text{Ca}$ , and  $\delta\text{D}$  values with other geochemical tracers to evaluate the role subduction has played in modifying the elemental budgets of mantle xenoliths from the Archean Slave Craton located in the Northwestern Territories, Canada.

### Sample Selection and Methods

We analyzed twelve garnet-bearing mantle xenoliths (11 lherzolites and 1 harzburgite) from the Diavik A154N and A154S kimberlite pipes located in the Lac de Gras area of the Slave Craton in the NWT, CA. Creighton et al. (2010) and Kilgore et al. (2020) have previously characterized these samples.

For isotopic analysis, mineral separates (olivine, clinopyroxene, and garnet) were hand-picked under a binocular microscope. Oxygen isotope ratios were measured via the laser fluorination method in the stable isotope laboratory at the Jackson School of Geoscience, University of Texas at Austin, using a ThermoElectron MAT 253 mass spectrometer.  $\delta^{18}\text{O}$  values are reported relative to standard mean ocean water (SMOW;  $\delta^{18}\text{O}_{\text{SMOW}} \equiv 0\text{‰}$ ). Clinopyroxene and garnet minerals were analyzed for their Ca isotope composition on the Scientific Triton TIMS at the University of Texas-Austin. The  $\delta^{40}\text{Ca}$  is reported relative to NIST SRM 915a. The hydrogen isotope ratios of hydrous, multi-mineral kelyphitic rims around garnets were determined by pyrolysis in a ThermoElectron MAT TC-EA, coupled to a ThermoElectron MAT 253 mass spectrometer located in the stable isotope laboratory at the Jackson School of Geosciences, University of Texas at Austin. All  $\delta\text{D}$  values are reported relative to SMOW (0‰).

## Results

The  $\delta^{18}\text{O}$  values of olivine ( $\delta^{18}\text{O}_{\text{olv}} = +5.33 \pm 0.13\text{‰}$ ;  $1\sigma$ ;  $n=12$ ) overlap typical mantle values.  $\delta^{18}\text{O}$  values of clinopyroxene and garnet ( $\delta^{18}\text{O}_{\text{cpx}} = +5.31 \pm 0.10\text{‰}$ ;  $\delta^{18}\text{O}_{\text{grt}} = +5.37 \pm 0.23\text{‰}$ ;  $1\sigma$ ) extend below those reported in most mantle peridotites. In general,  $\Delta^{18}\text{O}_{\text{cpx-olv}}$  and  $\Delta^{18}\text{O}_{\text{grt-olv}}$  are lower (avg. =  $-0.07\text{‰}$  and  $+0.05\text{‰}$ , respectively) than expected equilibrium values ( $\Delta^{18}\text{O}_{\text{cpx-olv}}$  from  $+0.30$  to  $+0.50\text{‰}$  and  $\Delta^{18}\text{O}_{\text{grt-olv}}$  from  $+0.40$  to  $+0.60\text{‰}$ ) at mantle temperatures from  $1200$  to  $1400^\circ\text{C}$ . Phlogopite-bearing kelyphitic rims have  $\delta\text{D}$  values (avg. =  $-126 \pm 13\text{‰}$ ;  $1\sigma$ ) lower than typical mantle values. The average clinopyroxene  $\delta^{44/40}\text{Ca}_{\text{cpx}}$  is  $+1.00 \pm 0.07\text{‰}$  ( $1\sigma$ ), within the range of the average MORB-source mantle. Garnet  $\delta^{44/40}\text{Ca}_{\text{grt}}$  values display a wider range than clinopyroxene ( $+0.99\text{‰}$  to  $+1.53\text{‰}$ ), with an average of  $+1.18 \pm 0.19\text{‰}$  ( $1\sigma$ ). Most garnets in this study have higher  $\delta^{44/40}\text{Ca}$  values than bulk peridotite values.

## Discussion

Subduction-related metasomatism is a reasonable explanation for non-mantle-like variations in the  $\delta^{18}\text{O}$ ,  $\delta^{44/40}\text{Ca}$  and the  $\delta\text{D}$  values of some xenoliths. In Figure 1, there are negative correlations between  $\delta^{18}\text{O}_{\text{cpx}}$  and  $\delta^{44/40}\text{Ca}_{\text{grt}}$  values ( $p\text{-value} = 0.148$ ) and between  $\delta^{18}\text{O}_{\text{grt}}$  and  $\delta^{44/40}\text{Ca}_{\text{grt}}$  values ( $p\text{-value} = 0.0056$ ) that trend from average mantle values ( $\delta^{18}\text{O}_{\text{cpx}} = +5.42\text{‰}$ ,  $\delta^{18}\text{O}_{\text{grt}} = +5.49\text{‰}$ ,  $\delta^{44/40}\text{Ca}_{\text{grt}} = +1.00\text{‰}$ ) to a reservoir with lower  $\delta^{18}\text{O}$  values and higher  $\delta^{44/40}\text{Ca}$  values ( $\delta^{18}\text{O}_{\text{cpx}} = +5.10\text{‰}$ ,  $\delta^{18}\text{O}_{\text{grt}} = +4.95\text{‰}$ ,  $\delta^{44/40}\text{Ca}_{\text{grt}} = +1.53\text{‰}$ ) which are end member values from this study. Smart et al. (2021) identified a similar negative correlation between  $\delta^{18}\text{O}_{\text{grt}}$  and  $\delta^{44/40}\text{Ca}_{\text{grt}}$  values in kimberlite-hosted eclogite xenoliths from the Kaapvaal Craton (Fig. 1; gray stars).

The lower  $\delta^{18}\text{O}$  values and higher  $\delta^{44/40}\text{Ca}$  values measured in this study (Fig. 1) are most likely explained by metasomatism by a melt or fluid derived from the lower-most portions of subducted altered oceanic crust. Altered oceanic crust has a slightly higher Ca isotope composition than the average mantle,  $\delta^{44/40}\text{Ca} = +1.03 \pm 0.19\text{‰}$ , and ranges from  $+0.54\text{‰}$  to  $+1.23\text{‰}$  (John et al., 2012; Blättler and Higgins, 2017). The bulk oxygen isotope composition of altered oceanic crust overlaps with average mantle values ( $\delta^{18}\text{O}_{\text{mantle}} = +5.2 \pm 0.3\text{‰}$ ; Matthey et al., 1994) and ranges from  $\sim+0$  to  $+5.5\text{‰}$  in altered sheeted dike complexes and ranges from  $\sim+6$  to  $+15\text{‰}$  in upper extrusive basalts (i.e., Gregory and Taylor, 1981). Therefore, recycled altered lower oceanic crust could produce the negative correlation between  $\delta^{18}\text{O}$  and  $\delta^{44/40}\text{Ca}$  values observed in the Slave Craton xenoliths. Smart et al. (2021) also attribute the negative correlation between  $\delta^{18}\text{O}$  and  $\delta^{44/40}\text{Ca}$  in the Bellsbank eclogite xenoliths to the recycling of altered oceanic (lower) crust. Recent metasomatism by fluids emanating from altered oceanic crust has also been invoked to generate Slave craton fibrous diamonds, especially those containing saline fluids (Weiss et al., 2015).

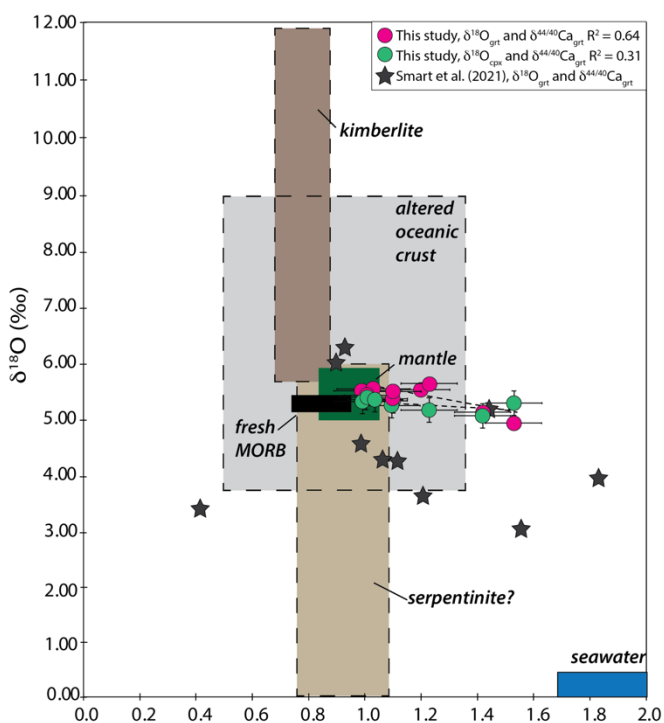


Figure 1.  $\delta^{18}\text{O}_{\text{grt}}$  (‰) versus  $\delta^{44/40}\text{Ca}_{\text{grt}}$  (‰) of from this study (pink circles) and  $\delta^{18}\text{O}_{\text{cpx}}$  (‰) versus  $\delta^{44/40}\text{Ca}_{\text{grt}}$  (‰) from this study (green circles) and  $\delta^{18}\text{O}_{\text{grt}}$  (‰) versus  $\delta^{44/40}\text{Ca}_{\text{grt}}$  (‰) of garnet minerals from Bellsbank eclogites from the Kaapvaal Craton from Smart et al. (2021). The typical range for  $\delta^{18}\text{O}$  and  $\delta^{44/40}\text{Ca}$  values of the reservoirs are from Smart et al. (2021) and references therein.

The low  $\delta D$  value of the kelyphitic rims (avg.  $= -126 \pm 13\%$ ) can also be explained by interaction with subduction-related fluids. Recent studies have found that subduction processes can fractionate the D/H ratio of Earth's reservoirs (i.e., Shaw et al., 2008). The water released from the subducting slab into the overlying mantle wedge is enriched in D, forming a D-depleted slab. The low  $\delta D$  values recorded in the kelyphitic rims from the Slave craton are consistent with fluids derived from deeply subducted slab residues that have lost some of their water during subduction-induced dehydration.

This recycled component was likely incorporated in the SCLM during the Mesozoic subduction of oceanic lithosphere beneath the North American continental lithospheric mantle. Oxygen isotope diffusion modeling can provide constraints on when the subduction-related metasomatism occurred, as inter-mineral oxygen isotope disequilibrium can be preserved in the mantle at temperature-dependent diffusive timescales. At these samples' high temperatures (1200 to 1350°C), clinopyroxene and garnet can only retain non-equilibrium  $\delta^{18}O$  values for  $<10^5$  years. This requires a subduction-related metasomatism event nearly the same age as the 55.4 Ma kimberlite eruption.

We propose three explanations for the temporal juxtaposition of metasomatism and kimberlite eruption: (1) kimberlite melts triggered remobilization of subduction-derived components in the SCLM, (2) the subduction-derived fluids/melt responsible for metasomatism were precursors to kimberlitic melts, or (3) the kimberlite melt itself was the metasomatizing agent. Ultimately, how or whether the subduction-related metasomatism recorded in the Slave craton mantle xenoliths reported in this study is related to kimberlite emplacement is unclear and cannot be answered with this dataset.

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