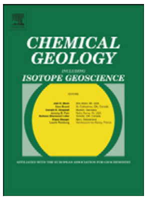
Chemical Geology 391 (2015) 83–89

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Nitrogen isotopic compositions and concentrations in MARID xenoliths

Sandeep Banerjee [a,*], T. Kurtis Kyser [a], Roger Mitchell [b]

[a] Department of Geological Sciences and Geological Engineering, Queen University, Kingston, Ontario, K7L 3N6, Canada
[b] Department of Geology, Lakehead University, Thunder Bay, Ontario, P7B 5E1, Canada

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 2 November 2014
Accepted 3 November 2014
Available online 14 November 2014

Editor: K. Mezger

Keywords:
Nitrogen isotope
Xenolith
Lithosphere
Mantle

ABSTRACT

Nitrogen isotopic compositions and concentrations in micas from kimberlite-hosted MARID (mica-amphibole-rutile-ilmenite-diopside) suite of xenoliths from the Kimberley area of the Kaapvaal Craton, South Africa, were measured using continuous-flow isotope-ratio mass spectrometry and Fourier transform infrared spectroscopy. Fourier transform infrared spectroscopy data suggest that the nitrogen in MARID phlogopite is from ammonium in the mica structure. The replacement of potassium by ammonium is the major mechanism for the storage of nitrogen within these phlogopites. The $\delta^{15}N$ values of micas from MARID xenoliths range from −11 to +9‰, and nitrogen contents range between 113 and 272 ppm. The ^{15}N enrichment of most samples relative to the average upper mantle $\delta^{15}N$ value of −5‰ suggests that the nitrogen reflects a recycled reservoir from subducted material within their source region. The presence of nitrogen from a recycled reservoir indicates that sedimentary organic nitrogen in the sub-continental lithosphere is not effectively cycled to the surface resulting in a geochemically heterogeneous upper mantle.

1. Introduction

Nitrogen is a major constituent in our atmosphere and a nutrient for most biota. However, estimates of the major terrestrial reservoirs of nitrogen indicate that nitrogen at the surface of the Earth is only about 30% of the total nitrogen of the Earth (Palya et al., 2011; Bebout et al., 2013a). Most of our knowledge about the isotopic composition of nitrogen in mantle reservoirs comes from studies of mid-ocean ridge basalts (MORBs) and diamonds. Although $\delta^{15}N$ values are variable in both materials, it is more extreme in the latter, ranging from −23 to +13‰ (Javoy et al., 1986; Boyd et al., 1987, 1988, 1992; VanHeerden et al., 1995; Cartigny et al., 1998; Hauri et al., 2002; Cartigny, 2005; Cartigny and Marty, 2013). Nitrogen contents in diamonds are also variable ranging from less than 10 to greater than 9500 ppm. Estimates of the $\delta^{15}N$ value of the convecting mantle sampled by MORBs are near -5 ± 2‰ (Marty and Humbert, 1997; Cartigny and Marty, 2013), identical to the mean value of diamonds, but nitrogen contents in MORBs are lower (<30 ppm) than in diamonds and complicated by degassing during emplacement (Marty and Zimmerman, 1999; Cartigny et al., 2001a).

Nitrogen contents and $\delta^{15}N$ values of common minerals in mantle xenoliths have also been measured, but nitrogen contents are low <26 ppm (Mohapatra and Murty, 2000; Yokochi et al., 2009). The range in $\delta^{15}N$ values from −27‰ to +13‰ measured in common silicate minerals from xenoliths are interpreted to reflect either mixing among mantle, air, and recycled sediments (Mohapatra and Murty, 2000) or nitrogen isotope fractionation during their crystallization (Yokochi et al., 2009). Recycled nitrogen has high $\delta^{15}N$ values of ca. >+4‰ based on studies of nitrogen isotopes in back-arc basin basalts (Sano et al., 1998, 2001) and minerals in metamorphic rocks associated with convergent plate margins (Bebout and Fogel, 1992; Bebout, 1995). The source of this heavy nitrogen is organic components in sediments that are subducted, but this sedimentary nitrogen may be variably partitioned into arc volcanism rather than subducting into the deeper mantle (Fischer et al., 2002).

In this study, we describe a continuous-flow isotope-ratio mass spectrometry (CF-IRMS) technique to measure the nitrogen contents and $\delta^{15}N$ values in micas from mantle xenoliths in kimberlites from South Africa. The technique has been used to examine nitrogen in micas from crustal sources (e.g. Jia and Kerrich, 2000), but analytical details are lacking and the technique has yet to be applied to mantle samples. The mantle xenoliths are part of the MARID suite (mica–amphibole–rutile–ilmenite–diopside), which consists of cumulates or metasomatized mantle associated with kimberlite or lamproite-like magmatism (Mitchell and Bergman, 1991; Sweeney et al., 1993; Konzett et al., 1998; Ulmer and Sweeney, 2002; Grégoire et al., 2002). The samples of MARID xenoliths in this study represent possible deep sources in the mantle, and unlike other xenoliths, contain major amounts of mica that are major repositories for nitrogen because of the presence of structural sites for ammonium (NH_4^+).

2. Samples and methods

2.1. Samples

Phlogopites were separated from eleven MARID suite xenoliths collected from the Bultfontein Dumps in Kimberley, South Africa. MARID

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* Corresponding author.
E-mail address: sandeep@geol.queensu.ca (S. Banerjee).

http://dx.doi.org/10.1016/j.chemgeo.2014.11.003
0009-2541/

xenoliths consist of variable modal abundances of two major minerals, phlogopite and amphibole, which constitute about 70–80 vol.% of the mineralogy. Other minerals include inhomogeneously distributed diopside, rutile, and ilmenite. In plane polarized light, amphibole grains are pleochroic from green- to- pale green and phlogopite grains are pleochroic from reddish brown- to- brown. Rutile and ilmenite are opaque minerals in transmitted light (Fig. 1A–F).

The xenoliths exhibit considerable variations in mineralogical assemblages and textural patterns. Phlogopite crystals exhibit random to strong orientation along their long axes and are present as two major size distributions, >1 mm and <0.3 mm (Fig. 1A). Diopside and amphibole occur as phenocrysts within bands of strongly orientated phlogopites (Fig. 1B). Diopside can occasionally include phlogopite. Some phlogopites also contain inclusions of opaque minerals and amphiboles (Fig. 1C). Opaque minerals typically are in close contact with phlogopites. Alternating bands of kinked phlogopite and amphibole are common within these xenoliths (Fig. 1E), with contacts between phlogopite and amphibole grains being either straight or irregular. Both phlogopite and amphibole can be enclosed by serpophite patches and exhibit corroded grain boundaries against serpophite (Fig. 1F).

The phlogopites typically have SiO_2 contents of 40.6–43.1 wt.%, TiO_2 of 0.2–2.4 wt.%, Al_2O_3 of 7.9–10.5 wt.%, FeO of 3.8–9.9 wt.%, MgO of 22–26 wt.%, CaO of <0.1 wt.%, and Na_2O of 0.05-0.2 wt.%. These phlogopites are potassium and fluorine-rich, with the potassium and fluorine contents ranging from 9.4 to 10.6 wt.% and 0.11 to 0.73 wt.%, respectively.

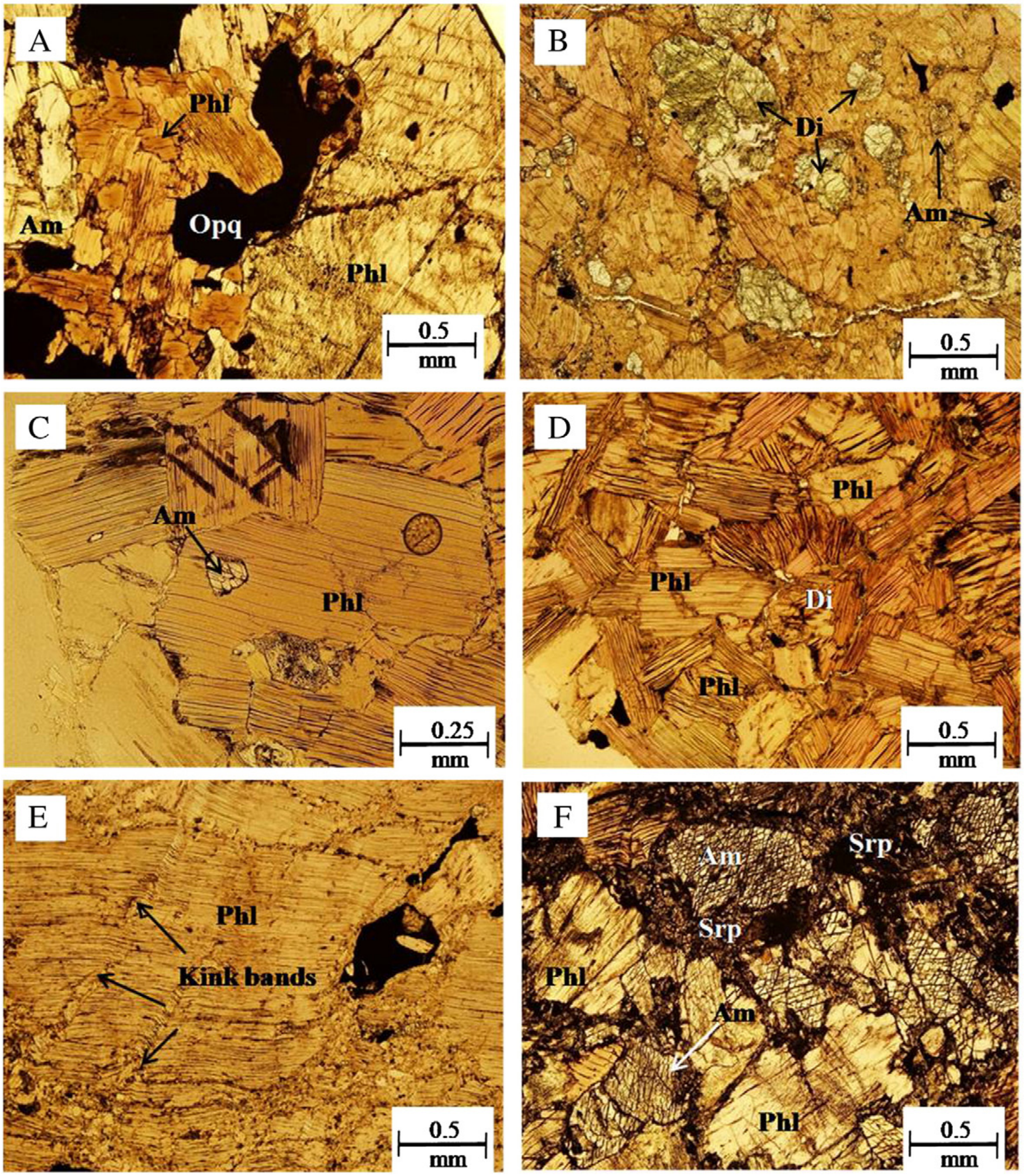

Fig. 1. Photomicrographs in plane polarized light of MARID xenoliths from the Bultfontein Dumps in Kimberley, South Africa. (A) Mar-12. Large and small subhedral lath-shaped red brown phlogopite (Phl) grains associated with amphiboles (Am) and opaque (Opq) minerals; the arrow points towards small phlogopites. (B) Mar-20. Diopside (Di) and amphibole (Am) grains within a band of strongly oriented phlogopites. (C) Mar-14. Amphibole (Am) inclusion within lath shaped brown phlogopite (Phl) grain. (D) Mar-15. Randomly oriented brown phlogopites surrounding a diopside (Di) grain, exhibiting interlocking texture. (E) Mar-18. Kink bands within phlogopite (Phl) grains. (F) Mar-14. Serpophite (Srp) patches surrounding subhedral amphibole (Am) and brown phlogopite (Phl) grains; note corrosion of phlogopites and amphiboles against serpophites.