The nature and scale of stable isotope disequilibrium in the mantle: ion and laser microprobe evidence

C. Graham
P. Kinny
B. Harte
J. Valley

Dept. of Geology and Geophysics, University of Edinburgh, Edinburgh EH9 3JW, UK.
Dept. of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin 53706, USA.

Introduction

The stable isotopes of oxygen and hydrogen in rocks are sensitive tracers of fluid-rock interaction processes, constraining the origins and fluxes of fluids (including melts). The spatial variations of these isotopic compositions constrain mechanisms of fluid transport and timescales of interaction and exchange processes. Knowledge of the oxygen and hydrogen isotopic composition of the Earth's mantle is based almost exclusively on conventional analyses of bulk-rock samples or mineral separates, in which isotopic information on the inter-grain and intra-grain scale is averaged, and the true range and scale of isotopic variations is obscured. Ion microprobe and laser probe techniques have been used to investigate stable isotopic variation and disequilibrium in mantle-derived xenoliths and megacrysts at the inter-grain and intra-grain scale, in order to constrain mechanisms of fluid-rock interaction and timescales of metasomatism and exchange.

Scales of hydrogen isotope disequilibrium in mantle amphiboles determined by ion microprobe

Conventional studies of mantle-derived magmas and hydrous minerals indicate 'normal' mantle δD values in the range -60 to -90‰ (SMOW). D-enriched compositions up to -20‰ in subduction-related volcanic glasses and amphibole-bearing xenoliths may reflect incorporation of D-enriched subduction-related fluid into the overlying mantle wedge. Ion microprobe study of pargasitic hornblendes from hornblende xenoliths from Hawaii (Deloule et al., 1991) detected an unusually D-depleted hydrogen component of -130‰ in hornblende rims, surrounding cores with normal mantle D/H. Large-scale mantle D/H heterogeneity is supported by data on the δD of kaersutite megacrysts (-133 to +8‰; Boettcher and O'Neil 1980, Dyar et al 1992).

We have determined the D/H of mantle-derived amphiboles using a Cameca ims-4f ion microprobe (cf. Deloule et al., 1991), with a spatial resolution of 20–30μm and a precision of better than 10‰ (1σ). Irregular K-richterite crystals up to 5mm in size from a kimberlite-hosted modally-metasomatized peridotite from Bultfontein showed a range in δD of 127‰, with one crystal showing irregular variation from -29 to -140‰ (Fig. 1), encompassing almost the entire spectrum of known mantle δD values. The irregular distribution suggests fluid-rock interaction proceeded along now-annealed grain fractures. These results support those of Deloule et al (1991)

K-RICHTERITE

Fig. 1. δD distribution in K-richterite crystals (colourless) in peridotite xenolith 47233, Bultfontein, S. Africa, determined by ion microprobe.
regarding the range of D/H and the scale of isotopic disequilibrium preserved in mantle-derived phases. By contrast, pargasite grains from two kimberlite-hosted metasomatized peridotite xenoliths were found to be isotopically homogeneous and strongly D-enriched relative to normal mantle values at $-26 \pm 6\%$ (Jagersfontein) and $-4 \pm 5\%$ (Monastery), consistent with a large component of subduction-related hydrogen.

Intra-grain and inter-grain $\delta D$ variation in mantle-derived kaersutite megacrysts from various world-wide localities spanned a range of compositions from $-24$ to $-130\%$. Cores of most kaersutite grains are isotopically homogeneous, but more D-enriched grains typically show mm or sub-mm scale zonation and D-enrichment in near-rim regions. Kaersutites from Deadman Lake, California, show inter-grain heterogeneity of about 40%. The simplest interpretation of these data is that metasomatized mantle source-regions from which the kaersutites are derived are homogeneous with respect to D/H on a centimeteric scale, but heterogeneous on a larger scale reflected in inter-grain and intra-locality variations. D-enrichment in megacryst rims may reflect magma-megacryst interactions during entrainment in the rising magma column.

Scales of oxygen isotope disequilibrium in a garnet peridotite determined by laser probe

Conventional oxygen isotope studies of coexisting minerals in peridotite xenoliths (Kyser et al. 1981) indicate oxygen isotopic disequilibrium between olivine and pyroxene, attributed to interaction of peridotite with metasomatic fluids (Gregory and Taylor 1986), in which olivine shows much greater variability in $\delta^{18}O$ than coexisting pyroxene. In order to establish the nature and scale of oxygen isotopic disequilibrium, we have applied a micro-sampling and laser probe technique to 500–600μm thick wafers of a high temperature, deformed garnet peridotite xenolith from the Jagersfontein kimberlite pipe, where xenoliths show evidence of high-T infiltration metasomatism. The xenolith contains olivine and orthopyroxene porphyroclasts and neoblasts, and large equant garnets.

Olivine and orthopyroxene porphyroclasts show inter-grain isotopic disequilibrium, and a comparable range of $\delta^{18}O$ from 4.8 to 6%. Olivine and pyroxene neoblasts (3.8–4.8%) are strongly $^{18}O$-depleted relative to porphyroclasts, and are inferred to have equilibrated with metasomatic fluid during deformation. Garnets show a wide range $^{18}O$, with one 3 × 4mm garnet showing irregular variation from 4.7 to 7.5%. Although large isotopic gradients are found on an intra-grain scale, local domain isotopic equilibrium amongst adjacent mineral grains is evident on a typical scale of a few mm. The $\delta^{18}O$ of orthopyroxene (but not olivine) porphyroclasts varies systematically with grain size consistent with diffusive exchange with a fluid of lower $\delta^{18}O$. Olivine appears to exchange oxygen by a recrystallisation mechanism involving neoblast formation.

While the sample shows inter-grain and intra-grain oxygen isotope disequilibrium, major and trace element compositions of phases determined by electron and ion microprobe are invariant. Oxygen isotope compositions are thus decoupled from elemental chemistry, suggesting that: (1) $^{18}O/^{16}O$ was externally buffered while elemental chemistry was internally buffered during fluid-rock interaction; or (2) exchange between peridotite and fluid was kinetically controlled, oxygen exchange being more rapid than elemental exchange; or (3) oxygen exchange occurred later, and perhaps at lower T, than elemental exchange.

In a separate ion microprobe study, a 1.5 × 1cm ilmenite megacryst from the Monastery kimberlite ($\delta^{18}O = 4.2\%$) has been shown to be isotopically homogeneous (+1.3%; n = 24) regardless of cracks, coarse exsolution and internal grain boundaries (Valley and Graham 1991).

Timescales of metasomatic exchange and eruption

Preservation of D/H and $^{18}O/^{16}O$ disequilibrium on a millimetric scale imposes severe time constraints on the processes of mantle metasomatic exchange and eruption of xenoliths and megacrysts, which may be calculated using available data for hydrogen diffusion in hornblende and oxygen diffusion in pyroxene. At mantle temperatures (1000–1200°C) D/H gradients would be undetectable on timescales of 10$^2$–10$^3$ years, although this figure is probably higher at low water activities. $^{18}O/^{16}O$ gradients would be erased on timescales of 10$^5$–10$^7$ years. Mantle exchange of D/H and $^{18}O/^{16}O$ between peridotite and fluid was thus closely associated in time with the magmatic event(s) that exhumed the samples.

References