

**MICRO-ANALYSIS OF D/H RATIOS IN MANTLE MINERALS BY CARRIER-GAS MASS SPECTROMETRY** J. O'Leary<sup>1</sup>, N. Kitchen<sup>1</sup> and J.M. Eiler<sup>1</sup>; <sup>1</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125, [eiler@gps.caltech.edu](mailto:eiler@gps.caltech.edu)

**Introduction:** Isotopic analysis of water released by vacuum heating of hydrous minerals and sub-marine basaltic glasses indicates that they vary in  $\delta D_{\text{SMOW}}$  between ca. +10 and -115 per mil (e.g., [1]). However, with few exceptions variations within that range are not well correlated with other geochemical and geologic properties and it is debated whether they reflect isotopic heterogeneity in the mantle, fractionations produced during ascent to the surface, or sub-solidus alteration. This ambiguity is at least partly due to the large sample size and slow rate of conventional analyses, which precludes linking isotopic ranges to grain-scale petrographic variables or constructing large data bases (many 10's of samples) in a reasonable period of time. Ion microprobe methods provide one solution to these problems, although they suffer from analytical uncertainties nominally 5 to 10 times worse than conventional measurements and large fractionations that can be a source of systematic error.

We describe here methods and initial applications of a new analytical approach to this problem involving laser- or resistance heating of 10's of micrograms of hydrous minerals and isotopic analysis of evolved water with accuracy and precision comparable to conventional measurements ( $\pm 2$  to 3 per mil). This technique is suitable for resolving grain-to-grain isotopic differences and coarse internal zonation of large individual grains; furthermore, it has a relatively rapid rate (~10 analyses per day) and can be used to generate large data sets. We describe an application investigating inter- and intra-crystalline heterogeneity of mantle phlogopites from South African kimberlites.

**Methods:** The core of our technique is a method for on-line reduction of water vapor carried in a He stream followed by carrier-gas mass spectrometry of evolved  $H_2$  gas [2]. Briefly, this technique is analogous to compound-specific analysis of C and H isotope ratios in organic matter and is appropriate for analysis of D/H ratios of  $\sim 5 \cdot 10^{-10}$  to  $\sim 5 \cdot 10^{-8}$  moles of water vapor with an external precision typically varying between  $\pm 1.0$  and  $2.0$  ‰ ( $1\sigma$ ). Under specific analytical conditions, this technique involves negligible analytical corrections ( $\sim 0-3$  ‰). This method can be used for analysis of water released from a variety of materials by several methods; we will emphasize measurements of water released during high-temperature pyrolysis of micas in a He-purged,  $SiO_2$ -glass, resistance-heated furnace.

External precision on  $\sim 50$   $\mu g$  aliquots of NBS-30 biotite varies from  $\pm 2$  to 5 per mil on any given day ( $n = 2$  to 9);  $\pm 2$  to 3 per mil is typical and increasingly common as we gain experience with the details of the method. We have no way of independently judging whether some of this variation reflects natural grain-to-grain heterogeneity but we think our average precision with this material is representative of true analytical uncertainties. There is no evidence for a significant analytical fractionation (i.e., differences between measured and nominal values) for this or other micas.

**Applications:** Previous ion microprobe studies suggest that mantle amphiboles and phlogopites are often zoned in  $\delta D$  by 10's of per mil (and occasionally by as much as 150 per mil; e.g., [3]) over length-scales of several hundred microns to several millimeters; such variations should be easily observed using our technique as differences in  $\delta D$  between mechanically micro-sampled cores and rims of individual grains and/or as differences in  $\delta D$  between co-existing large and small grains. We have searched for such inter- and intra-crystalline heterogeneity in samples of mantle phlogopite previously analyzed for bulk hydrogen isotope composition by [1]. Measurements of sample Kb-5-10 reveal only a vanishingly small difference in  $\delta D$  between cores and rims of individual  $\sim 2$  mm-diameter grains ( $-73.8 \pm 1.5$  vs.  $-69.8 \pm 2.0$  ‰, respectively; the nominal bulk  $\delta D$  of phlogopite in this sample is  $-65$  ‰ [1]). Additional work is needed to understand what (if any) general significance this result has, although at face value our data reveal no evidence for complex internal zonation in the D/H ratios of mantle minerals.

**References:** [1] Boettcher and O'Neil, 1980, *AJS* 280-A, 594-621; [2] Eiler and Kitchen, submitted to *GCA*; [3] Deloule et al. 1991 *EPSL* 105, 543-553.