We present a method for on-line dehydration of small quantities of hydrous and nominally anhydrous minerals followed by measurement of the absolute abundance of hydrogen released from the sample by continuous-flow mass spectrometry. This method is appropriate for measuring water content between 18 ppm and 10 wt% H2O and requires a minimum of ~2 × 10^-8 of hydrogen per analysis. The hydrogen needed for an analysis corresponds to 10–200 µg of hydrous minerals or 5–40 mg of nominally anhydrous minerals. We develop measurement protocols for garnet and pyroxene, two nominally anhydrous minerals that are potentially major reservoirs of hydrogen in the mantle.

**Keywords:** Hydrogen, hydrogen analysis, water content, continuous flow mass spectrometry, nominally anhydrous minerals, IRMS

**INTRODUCTION**

Hydrogen is a nearly ubiquitous component of geologic materials (Aines and Rossman 1984; Andrut et al. 2003; Bell et al. 1995; Bell and Rossman 1992a, 1992b; Bromiley and Bromiley 2006; Ingrin and Skogby 2000; Johnson and Rossman 2004; Skogby et al. 1990; Smyth et al. 1991; Vlassopoulos et al. 1993; Woodhead et al. 1991) and has a disproportionately strong effect on mineral rheology (Karato et al. 1986; Mackwell et al. 1985), melting temperature (Hirose and Kawamoto 1995), electrical conductivity (Karato 1990), and other physical and chemical properties (Mei and Kohlstedt 2000a, 2000b). Experimental determinations of the solubility of hydrogen in minerals at elevated temperatures and pressures have shown that common silicates (e.g., olivine, pyroxenes, feldspars, and garnet) at deep-crustal and mantle conditions can contain up to thousands of parts per million (weight fraction, as H2O) (Bromiley and Bromiley 2006; Mosenfelder et al. 2006). However, most natural minerals measured to date contain far less than their saturated hydrogen contents—a few hundred parts per million is typical. Quantification of such low hydrogen contents is a challenge, particularly for materials that are precious, limited in availability, or compositionally zoned.

Hydrogen contents of minerals have been previously determined using vacuum manometry (Bell et al. 1995; Holdaway et al. 1986; Ihinger et al. 1994; Rossman and Aines 1991), infrared absorption spectroscopy (Ingrin and Skogby 2000; Beran and Libowitzky 2006; Libowitzky and Rossman 1997; Paterson 1982; Rossman and Smyth 1990; Smyth et al. 1991), secondary ion mass spectrometry (Aubaud et al. 2004; Hauri 2002; Holdaway et al. 1986; Koga et al. 2003), and nuclear reaction analysis (Bell et al. 2003, 2004; Hammer et al. 1996; Lanford 1978; Maldener et al. 2001, 2003; Rossman et al. 1988). Each of these methods has strengths and weaknesses: vacuum manometry is quantitative (i.e., it requires no independent standardization to determine absolute hydrogen concentrations), but typically requires ca. 1–5 µmoles of hydrogen (as H2) corresponding to gram quantities of hydrogen-poor materials. Such large amounts of sample increase the risks of contamination and often cannot be obtained. Infrared absorption spectroscopy constrains the chemical environment of hydroxyl groups and water molecules in mineral structures, and is both sensitive and precise as a measure of hydrogen concentration, but requires independent calibration using a quantitative technique. Such calibrations are available only for a few minerals, depend on orientation, and may not be appropriate for extrapolation outside of the concentration range of their calibration (Cho and Rossman 1993; Rossman and Aines 1991). Secondary ion mass spectrometry can be sensitive and precise (Bell et al. 2003), consumes exceptionally small amounts of material for analysis (typically picograms; Koga et al. 2003), and is appropriate for studies of compositional zonation in solids at scales down to tens of micrometers (or possibly smaller using NanoSIMS instrumentation; Floss et al. 2006). However, SIMS also requires independent calibration using a quantitative technique, and calibration is highly specific to mineral type and chemical composition. Nuclear reaction analysis is quantitative and can yield finely resolved depth profiles of hydrogen concentration, but is technically difficult, not widely available, and is a near surface technique that cannot be compared easily to bulk techniques for some materials.

We present a new technique for measuring the abundance...