

Micro-analysis of absolute water concentration in minerals

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Abstract

Accurate water concentrations in hydrous and nominally anhydrous minerals are necessary for describing both the size of reservoirs in the global water cycle and the transfer processes between those reservoirs. We present a new method for the determination of absolute hydrogen abundance in solid materials. Hydrogen extraction and manometry is a standard technique for absolute water content measurements, but requires large masses of sample (typically 10's of mg to grams). Major contributions have been made by measuring relative concentration on very small samples using Fourier transform infrared (FTIR) spectroscopy and secondary ionization mass spectrometry (SIMS) but these methods must be calibrated by absolute methods. Our method allows absolute determination of hydrogen content while reducing sample sizes by two to three orders of magnitude, requiring less than 100 μg of materials with 1 wt% H_2O and less than 10 mg for those with 1000 ppm H_2O . This micro-analytical technique will allow the measurement of samples that were previously impractical or impossible to measure by current techniques. Our method uses continuous flow mass spectrometry to measure mols of hydrogen. Mineral samples are dehydrated by combustion in a flow of helium carrier gas. Water is cryogenically collected, converted by uranium reduction to hydrogen gas, and analysed by isotope ratio mass spectrometry (IRMS). The measured signal intensity of H_2^+ ion current is calibrated by repeated analyses of the mineral zoisite, which contains a stoichiometric concentration of 1.98 wt % water. Signal response is linear over the calibrated range of 62 to 809 nmols, with scatter about the line of $\pm 6\%$ ($n = 8$). In the course of this analysis the hydrogen isotopic ratio is also determined. For our Tanzanian zoisite samples the average $\delta D = -37.5 \pm 1.2$ per mil ($n = 8$). This system is flexible enough to work with a variety of minerals and other geologic materials. For each material a proper heating protocol must be developed. We use Raman and FTIR spectroscopy to establish that samples are not dehydrated during pre-treatment to remove surface water and that samples are completely dehydrated after combustion. These methods have confirmed that we successfully dehydrate samples of zoisite, basaltic glass, tourmaline, and garnets in 30-90 minutes. Duplicate analyses of a tourmaline sample (expected H_2O content of ~ 4.0 wt. %) give a measured value of 3.76 ± 0.04 %. Repeated analyses of ALV 526-1, a mid-ocean ridge glass with a known water content of 0.21 wt % water, yield a value of 0.21 ± 0.06 wt % ($n = 10$) total water contents ranging from 43-181 nmols. The high relative error for ALV 526-1 is a result of uncertainties introduced by blank corrections or by surface water contributions. These are issues that must be addressed with continued work. The small sample sizes required by this analysis open up possibilities for studies of many phases of interest in mantle geochemistry. The water contents of mantle pyroxenes and garnets are within a range where 5-50 mg of sample is adequate for analysis. These measurements will help describe the mantle water budget, one of the least understood components of the global hydrologic cycle.

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