A new method to determine both water content and hydrogen isotope composition of two forms of water in nominally anhydrous minerals

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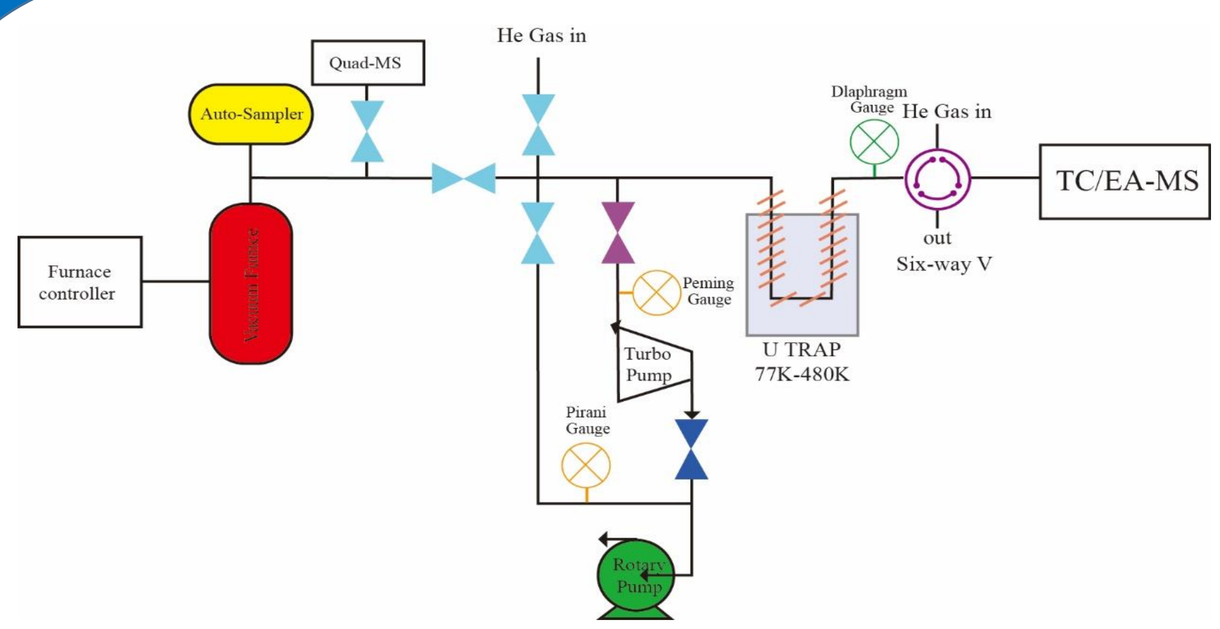

Fig. 1 Schematic of high vacuum stepwise-heating (HVST) system

Introduction

The two forms of water in NAMs, together with water in hydrous minerals, make up the reservoirs of water in the interior of Earth. In this study, we have developed a high vacuum stepwise-heating device (HVST) (Fig. 1), which ensures stepwise releasing different forms of water from NAMs by determining the releasing temperatures for different forms of water in NAMs. Our results demonstrate that the online technique combining HVST and TC/EA-MS (HVST-TC/EA-MS) can distinguish the different forms of water in NAMs.

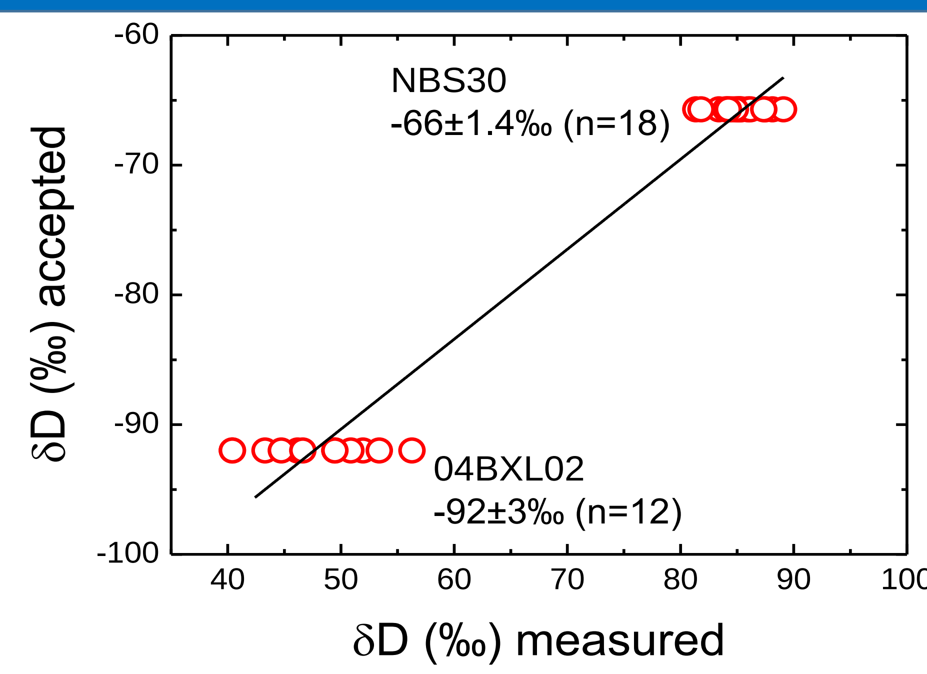

Fig. 2 δD values measured by HVST-TC/EA-MS for two standards materials (biotite NBS-30, δD = –65.7‰; garnet 04BXL02, δD = –93‰), plotted as a function of the measured δD value for each standard.

Standardization

In the HVST-TC/EA-MS online analysis, the δD value of the reference gas is assumed to be 0‰ (SMOW). Corrections were made using a linear regression of the measured values compared to expected values for NBS-30 biotite and 04BXL02 garnet (Fig. 2). The regression equation is given by: $\delta D_{accepted} = 0.69345\delta D_{measured} - 125.02606$. The relationship between the measured and accepted δD values is linear with a R^2 value of 0.97516.

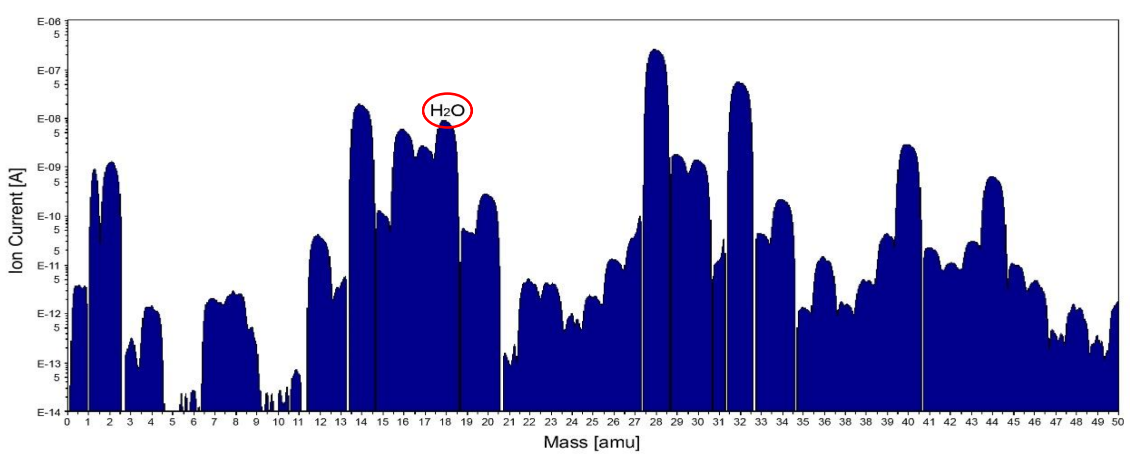

Fig. 3 Signal intensity of residual gases under vacuum of 10^{-3}Pa. The signal intensity of molecular mass of 18 represents the background of water vapor, and is about 1×10^{-8}A.

Monitoring the dehydration

In order to ensure that the two forms of water in NAMs can be released step by step under vacuum, the key is to determine the releasing temperature of the two forms of water in NAMs. In our study, the on-line quadrupole mass spectrometer in the HVSH device can be used to monitor the dehydration process of garnet at different temperatures. the signal intensity of molecular mass of 18, which indicates the background of water vapor in vacuum system, is about 1×10^{-8} A.

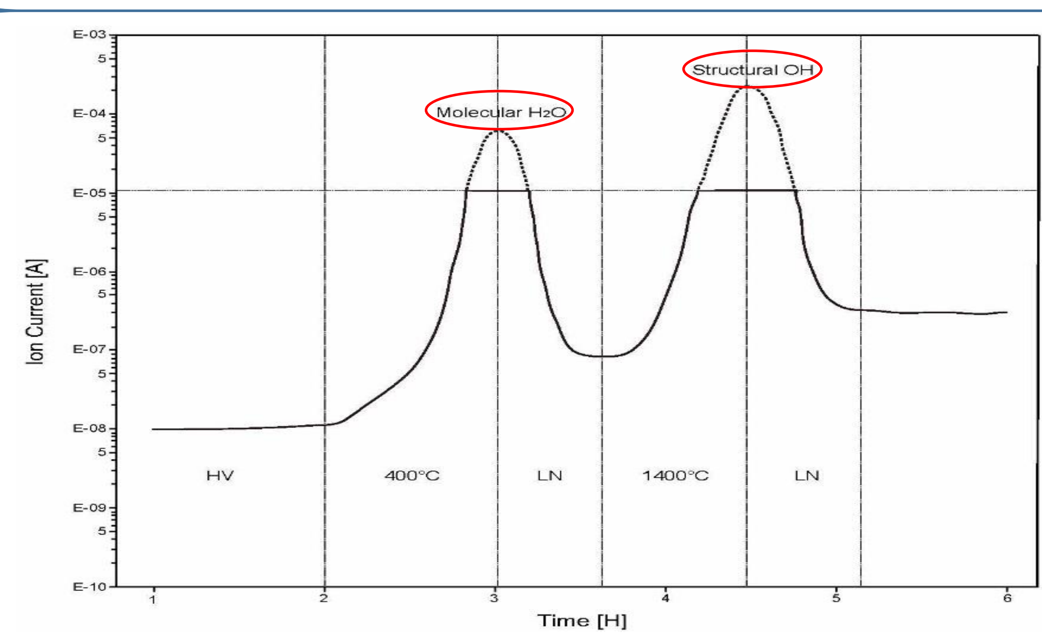

Fig. 4 Dehydration of different forms of water in garnet recorded by on-line quadrupole mass spectrometer under different heating temperatures. HV: high vacuum of 10^{-4}Pa; LN: liquid nitrogen freezing; 400°C and 1400°C: heating temperatures.

Determining the dehydration temperatures

Water peak increases with temperature up to 400°C (Fig. 4), indicating that molecular water begins to liberate from garnet at 400°C. Water peak increases again with increasing the heating temperature from 400°C to 1400°C (Fig. 4), indicating that the releasing temperature of structural OH is profoundly higher than that of molecular water.

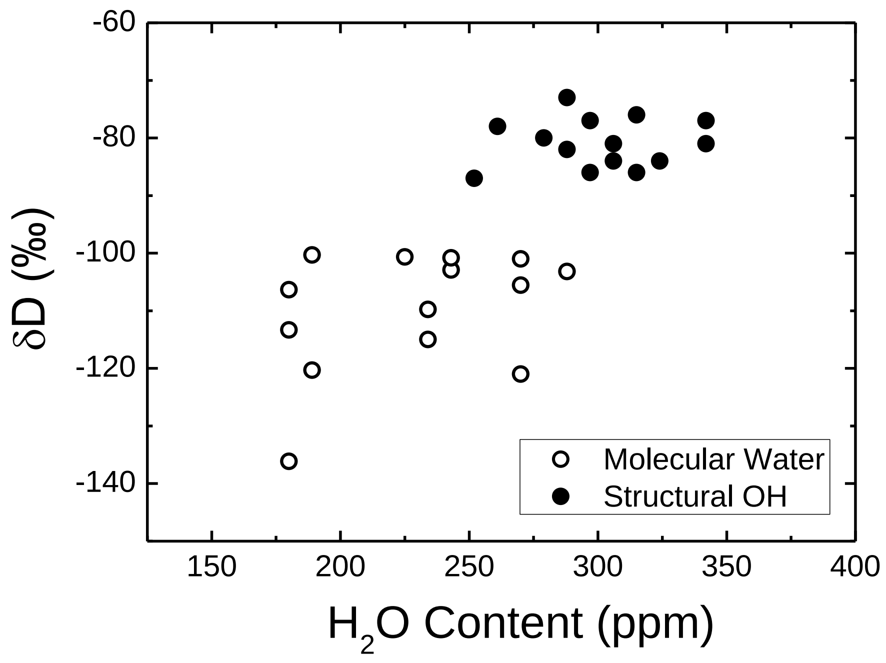

Fig. 5 Comparison of water concentrations and H isotope compositions between molecular water and structural OH in garnet 04BXL02.

Molecular H_2O and structural OH in NAMs

As presented Fig. 5, garnet 04BXL02 gives molecular H_2O content of 228±39 ppm and a δD value of –110±10‰ at 400°C for 1 hour. At a higher heating temperature of 1400°C for 1 hour, garnet 04BXL02 shows structural OH content of 301±27 ppm and a δD value of –81±4‰.

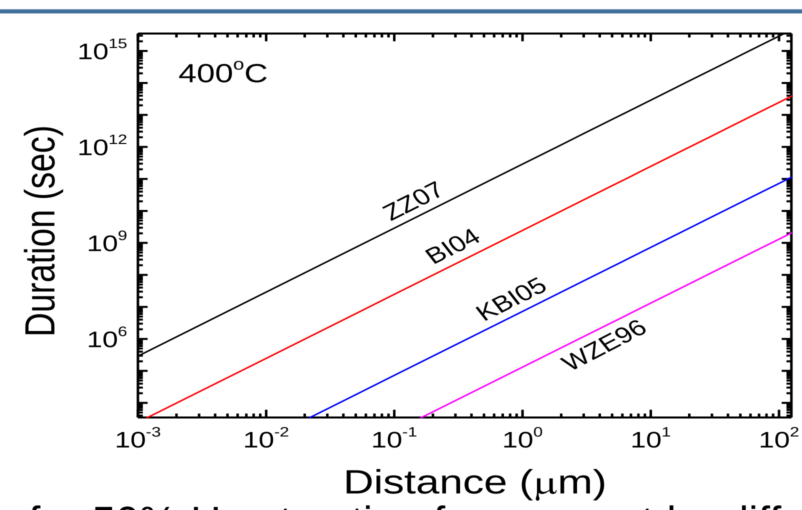

Fig. 6 Timescale for 50% H extraction from garnet by diffusion in different grain sizes at 400°C. Timescale was calculated at multi-direction diffusion conditions. The four curves were calculated by using four sets of diffusion coefficient, which are abbreviated as ZZ07 for Zhao and Zheng (2007), BI04 for Blanchard and Ingrin (2004), WZE96 for Wang, Zhang and Essene (1996), and KBI05 for Kurka, Blankchard and Ingrin (2005).

Diffusion of H

In our study, the uncertainty is whether the structural OH could be lost from the garnet when heating it at 400°C for releasing of the molecular water. This can be evaluated by using known kinetic data for the diffusion of H in garnet. It generally obeys the diffusion "rule of thumb" equation: $r \approx [5(Dt)^{1/2}]/2$. The timescale calculations indicate that loss of the structural OH from the garnet would not occur during heating garnet at 400°C for 1 hour for releasing of the molecular water.