Development for in-situ Volatile Element Abundances, and Hydrogen and Sulfur 2-Isotope Analyses of Silicate Glasses by SIMS.

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Introduction: Enrichment or depletion of water and other volatile elements significantly affect igneous processes occurred in the protoplanetary disk and the interior of planets/planetesimals, resulting diversity of inclusions in chondrites and the surface and internal evolution of planets. Due to high mobility and reactivity of volatile elements, however, it is difficult to correctly trace abundances of volatile elements in source materials and their behavior in igneous processes. Glass is one of major phases to contain volatile elements. Since glass is highly susceptible to later aqueous and/or thermal processes, it is important to measure volatile elements in pristine glasses such as a melt inclusion encapsulated in robust minerals. We developed in-situ analysis techniques of volatile element abundances (CO_2, H_2O, F, Cl, S, and P_2O_5) of silicate glasses, and hydrogen (D/H) and sulfur 2-isotope ($^{34}S/^{32}S$) analyses for silicate glasses with abundant water ($\gtrsim 0.2$ wt.%) and sulfur ($\gtrsim 500$ ppm) contents.

Analytical procedures and results: In-situ analyses were performed with an ion microprobe, CAMECA IMS 1280-HR at Kochi Institute, JAMSTEC. For accurate measurements of volatile element abundances, we established homogeneous standard glasses (EPR-G3, IND-G1, IND-G2, FJ-G2, and MRN-G1) [1]. We also used several synthetic glasses for calibration and the ranges of volatile elemental abundances measured standard glasses are 97 - 9400 ppm for CO_2, 0.020 – 4.8 wt% for H_2O, 55 - 2957 ppm for F, 51 - 1372 ppm for S, 55 - 2833 ppm for Cl, and 0.084 - 0.41 wt% for P_2O_5, respectively [1]. the synthetic quartz glass, HERALUX-E-LA, was used to check back ground signals. The samples were polished using alumina lapping films (down to #10000; 0.5μm) and were pressed onto the indium metal loaded in a 1-inch diameter Al-metal cup.

Volatile abundances were measured using a 20 kV Cs^+ ion primary beam (300 to 500 pA and ~10 μm in diameter). Secondary ions ($^{12}C^-$, $^{16}OH^-$, $^{19}F^-$, $^{31}P^-$, $^{32}S^-$, $^{35}Cl^-$, and $^{30}Si^-$) were accelerated at -10 kV and detected by an axial electron multiplier (EM) detector using a magnetic peak switching method. To reduce contribution of surface contamination, we set the field aperture at 5×5 μm of the field of view and cut ion signals from the edge of the primary beam. Mass resolving power (MRP, M/ΔM) was set at 6000. Volatile element signals were normalized to the $^{30}Si^-$ signal. We performed multiple sessions to obtain the calibration lines. We applied a power-law regression for the CO_2 calibration and a linear-law regression for other volatile elements. The range of session-to-session variation of slopes of calibration lines is about 10% for 4 years (e.g., Figure 1). Reproducibility of the standard glass (EPR-G3) measurements in each measurement session is typically 1-2% for all volatile elements. It should

Figure 1: Calibration lines for H_2O content in basaltic glasses determined in 5 separate measurement sessions. (from [1])

be noted that sufficient pre-pumping (>12 hours before measurement) in the high-vacuum storage chamber and complete removal of epoxy are desirable for accurate H_2O content and hydrogen isotope analyses.

For hydrogen and sulfur 2-isotope analyses, we employed a FC-EM detector setting to achieve quick and accurate analyses for H_2O- and/or S-rich samples. Primary Cs^+ beam conditions are ~5 nA and ~15 μm in diameter for hydrogen isotope analysis, and ~0.5 nA and ~10μm in diameter for sulfur 2-isotope analysis, respectively. Details in analytical conditions were described in [2]. Hydrogen isotope ratios were determined by simultaneously detected $^{16}OH^-$ (FC, MRP~5000) and $^{16}OD^-$ (Axial EM, MRP~10000) signals. Although the instrumental fractionation was large (~+600‰), we could achieve the spot-to-spot reproducibility (2 SD) of ~±6‰ for basaltic glasses with >1 wt% H_2O and ~±12‰ for natural abyssal basaltic glasses with ~0.2 wt% H_2O [2]. Sulfur 2-isotope ratios were determined by simultaneously detected $^{32}S^-$ (FC, MRP~2200) and $^{34}S^-$ (Axial EM, MRP~5000). The spot-to-spot reproducibility (2 SD) of the standard glass (EPR-G3, [S]=1269 ppm) was ~±0.7‰ [2]. Com-

Figure 2: The image of a melt inclusion in olivine with volatile (V), hydrogen isotope (H), and sulfur isotope (S) measurement pits. (modified from [2])

bined with these analytical techniques, we can measure volatile element abundances, hydrogen, and sulfur isotope ratios of melt inclusions as small as 30 μm in size (Figure 2). By employing an EM-EM detector setting, we expect to extend our techniques for studies on extraterrestrial samples with much lower volatile contents (e.g. [3]).

References: [1] Shimizu K. et al. (2017) *Geochemical Journal* 51:299-313. [2] Shimizu K. et al. (2019) *Geochemical Journal*: in pre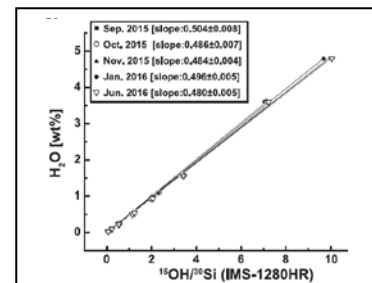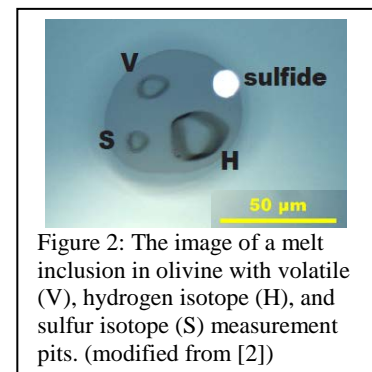ss. [3] Hauri E. H. et al. (2011) *Science* 333:213-215.