SPATIALLY CORRELATED ANALYSES OF HYDROGEN ISOTOPE COMPOSITIONS AND IRON VALENCE IN DISH HILL KAERSUTITES: IMPLICATIONS FOR MARTIAN IGENOUS SAMPLES.

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Introduction: We are investigating microscale variations in D/H ratios, water abundances and Fe valence in carefully characterized terrestrial igneous samples with the goal of understanding the variability in hydrogen isotope compositions and redox within and among the martian meteorites. A large suite of kaersutite megacrysts was collected from the Dish Hill alkali basalt volcano in southeastern California; of these, 17 have been well characterized with the electron microprobe [1]. These megacrysts span a range in Mg# with systematically correlated minor and trace element abundances. Bulk water contents and D/H ratios were previously determined for these 17 kaersutites by vacuum line manometry and gas source IRMS [1].

Analytical Methods: In this study, we selected a subset of the well-characterized Dish Hill kaersutites (DSH 34, 40, 41, 53, 54 and 55) for co-located microscale analyses of hydrogen isotope systematics and iron valence. Secondary ion mass spectrometry (SIMS) measurements of D/H ratios and H_2O concentrations in these kaersutites were performed on the Cameca IMS-6f at Arizona State University. A Cs^+ primary beam of ~10 nA was rastered on a 30×30 μm^2 surface area. A field aperture set the analyzed area to 15 μm diameter, which reduced background associated with hydrogen adsorbed to the sample surface at the edge of the sputtered crater. Presputtering was performed for ~5 min prior to analyses. Each measurement comprised of 50 cycles of measuring H^- and D^- ions with counting times of 1s and 10s, respectively. At the end of each measurement, $^{16}O^-$ was measured. The H_2O contents were determined using a $H^-/^{16}O^-$ vs. H_2O calibration based on three terrestrial amphiboles: Kipawa, Bamble and Mont Emma (Deloule et al., 1991). The instrumental mass fractionation (IMF) factor was calculated based on analyses of these same amphibole standards. The background for H_2O concentrations was determined using the $H^-/^{16}O^-$ ratio measured in San Carlos olivine and was subtracted from the H_2O concentration estimated for each kaersutite measurement.

The Fe K XANES spectra were collected on spots adjacent to the SIMS pits on each of the Dish Hill kaersutites studied here using the GSECARS X-ray microprobe at the Advanced Photon Source at Argonne National Lab. Analysis spots (~ 1 μm) were ~ 30 μm from the edge of the SIMS pit and spectra were collected with the kaersutite grain at four different orientations, accomplished by rotating the sample mount through 90 degree increments. Three different valence determination methods were applied to each spectrum [2]. The "Centroid" method used the centroid energy of the pre-edge multiplet and was calibrated using amphibole spectra collected using the X26A X-ray microprobe at NSLS-I (Brookhaven Nat. Lab.) on 44 amphibole samples which were also analyzed by Mössbauer. The "PLS" (partial least squares) method used a comparison of the full spectrum with those standards. The "Lasso" (least absolute shrinkage and selection operator) method is an ordinary least squares regression model using only those energies in the standard spectra that are most sensitive to valence. For each spot and each method, valence was determined for the spectrum from each of the 4 orientations and those were averaged. The average valences for the three methods were in good agreement. The results using the Lasso method produced the smallest standard deviations for the different orientations and those values are reported here.

Results and Discussion: The water (H_2O) abundances measured via SIMS in the DSH kaersutites range from 0.7 to 1.8 wt.% while the δD values vary from -168 ± 84 ‰ to +538 ± 155 ‰ and are anti-correlated. The Fe valence, defined as "2 + ($Fe^{3+}/\Sigma Fe$)", in most kaersutites analyzed here (DSH 40, 41, 54 and 55) is identical (2.43 ± 0.02; 2SD), so the variation in water content and δD in these samples may be attributed largely to subsolidus diffusion and loss of H_2O. However, the Fe valence in DSH 34 is higher (2.52 ± 0.04), while that in DSH 53 is on average still higher and shows resolvable variation (2.50 ± 0.01 to 2.58 ± 0.02). Petrologic and geochemical evidence suggests that the higher Fe valence in DSH 34 may be from wall-rock assimilation. In contrast, the Fe valence in DSH 53 is anti-correlated with H_2O content and correlated with δD, indicative of dehydrogenation of its parent magma. These results suggest that combined H_2O-δD-$Fe^{3+}/\Sigma Fe$ systematics are likely to provide valuable insights into the petrogenesis of the martian meteorites, some of which may also have experienced similar processes (e.g., assimilation, dehydrogenation, and subsolidus diffusion) on Mars.

References: [1] Bell, D. R. and Hoering, T.C. (1994) *Conference on Deep Earth and planetary volatiles,* Pasadena, CA, LPI Contribution: p.4. [2] Dyar, M.D., Speicher, E.A., Gunter, M.E., Lanzirotti, A., Tucker, J.M., Carey, CJ, Peel, S.A., Brown, E.B., Oberti, R., and Delaney, J.S. (2016) *Amer. Mineral.,* 101, 1171-1189.