THE ROLE OF DEHYDROGENATION ON THE HYDROGEN CONTENTS AND δD VALUES OF KAERSUTITES

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Introduction: Kaersutite (Ti-rich amphibole) is found in melt inclusions in martian meteorites and may be used to constrain the martian mantle H content and δD value [e.g., 1-6]. Kaersutites from Zagami, Shergotty and Chassigny have very high and variable δD values [510-1880 ‰ rel. to SMOW; 2]. The variation in δD values in martian minerals may result from: 1) exchange between the martian atmosphere and a mantle or magmatic reservoir [7]; 2) shock processes [8]; 3) exchange between the martian atmosphere and terrestrial water [9]; and, 4) dehydrogenation [H$_2$-loss; 10] through either equilibration or diffusive processes during ascent and emplacement following [10, 11]:

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \tfrac{1}{2} H_2 \qquad (1)$$
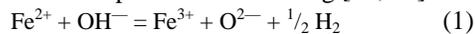
Dehydrogenation of kaersuitite is favored above 700°C, and the preferential loss of ^1H causes the δD values of the kaersutite to increase [e.g., 12]. To evaluate the δD variations in martian kaersutites, we analyzed D/H ratios and H contents in natural and heat-treated Ti-rich amphiboles on the milligram (conventional) and nanogram (ion microprobe, SIMS) scale. [Herein, we use H to refer to the H content of the amphiboles, but we note that it was measured as H$^+$ with SIMS and H$_2$ using conventional techniques and H is reported as H$_2$O (~OH atomic formula units) in the figures below.]

Samples: Amphiboles were collected from rapidly cooled dikes and maars and from rocks that cooled more slowly or were stored in a subsurface magma chamber before eruption (lava flows and cinder cones) [10]. The samples are Ti-pargasites to kaersutites with minor intracrystal major element variation [10]. The rapidly cooled samples in general have higher and homogeneous H, while the slowly cooled samples have lower and heterogeneous H [10].

Fragments from a single kaersutite megacryst BD4 were heat-treated to evaluate mechanisms of H-loss. This sample was considered relatively homogeneous in major elements and H [10], although subsequent analyses show a range in H (below). Different aliquots of BD4 were heated in a vertical furnace at ~800 °C in air for 30-309 min and cooled to room temperature to minimize crystal shattering.

Analytical methods: Bulk H and D/H ratios were measured on the BD4 and SS6 samples at the University of Tübingen, following conventional techniques described elsewhere [13]. We analyzed major elements (ASU and UWO JEOL JXA 8600 electron probes), D/H (ASU Cameca 6f SIMS) and H (ASU Cameca 6f and 3f SIMS) on approximately the same 15 μm location in each natural crystal. The Cameca 6f procedures were similar to [8]. We analyzed background controls and high H-low δD Ti-pargasites and kaersutite standards (H$_2$O>0.8 wt.%) at the beginning and end of each session and where possible after four amphibole analyses. The H$_2$O content was determined for the same spot as the δD values using $^1H/^{28}Si$ versus H$_2$O curves.

Results: The SIMS results for rapidly cooled, natural amphiboles give relatively low δD values with high H (Fig. 1); these values are near the accepted 'mantle values' [14]. In contrast, the slowly cooled, natural amphiboles have variable δD and H, and some have very high δD values (Fig. 1). The data cannot be ascribed to hydrothermal alteration or weathering (Fig. 1), but are consistent with dehydrogenation.

The heat-treated kaersutites have δD-H values near the range of the slowly cooled samples, consistent with dehydrogenation (Fig. 1). The scatter in the heat-treated data (Fig. 1) is probably due to variation in the H of the BD4 starting material (Fig. 1), and defects or cracks in the crystals. The H and δD values correlate linearly with the square root of the run duration indicating equilibrium dehydrogenation.
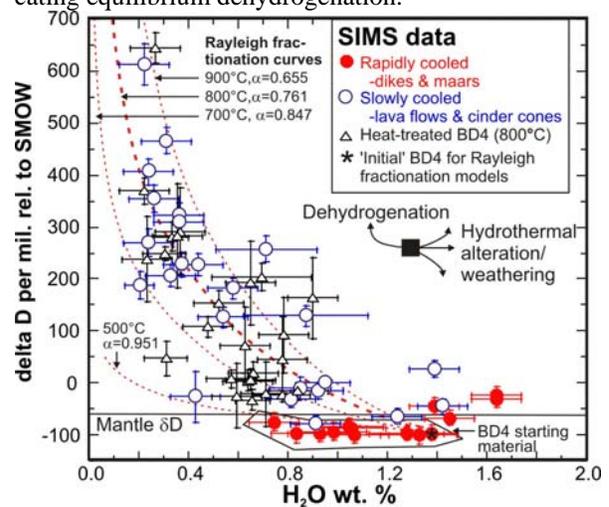

Fig. 1: SIMS δD vs. H$_2$O for natural samples (rapidly and slowly cooled) and heat-treated samples. Rayleigh fractionation curves using theoretical αs are shown for a range of Ts.

Evaluation of the SIMS analysis technique: Because very high δD values have not been reported for Ti-rich amphiboles analyzed with conventional techniques, we verified the SIMS δD values using multiple approaches. 1) We produced the same data array over four separate analytical sessions with two different operators. 2) We confirmed that the instrumental mass fractionation and composition were not correlated [cf. 15]. 3) We determined that the background corrections and standard calibration had no significant effect on the SIMS data (beyond the errors for an individual point). 4) We compared SIMS and conventional analyses for BD4 and SS6. For the relatively homogeneous crystal BD4, the conventional and SIMS analyses are within error for δD, but SIMS H contents range to lower values than those obtained conventionally (and by [10]) (Fig. 2A). In contrast, for the heterogeneous SS6 sample, the conventional and SIMS analyses do not agree; SIMS analyses have lower H and higher δD values (Fig. 2A). Mixing calculations (Fig. 2B) show that the differences between the SIMS and conventional analyses may be entirely explained by the relative contributions from H-poor and H-rich components in the crystal. In the conventional analysis, the δD value is biased towards the higher-H component of the crystal, which contributes disproportionately to the bulk δD analysis (e.g., F>~0.2 for the hypothetical mixing curves in Fig. 2). Small-scale SIMS analysis (nanogram scale) will give a larger range of δD values and H in heterogeneous minerals than a conventional analysis (milligram scale). These results show the importance of using high-H calibration standards for SIMS H and δD analysis.

Rayleigh fractionation model for dehydrogenation. Both the experimental and natural data may be explained in terms of Rayleigh fractionation due to loss of $H_2(g)$ from dehydrogenation. Our data for the heat-treated BD4 samples are best fit to the equation (e.g., [16]): $\delta D_f - \delta D_i = (1000 + \delta D_i)\,(F^{(\alpha-1)} - 1)$ (2) with an α value of 0.778, where F is the fraction reacted, i is the initial value (most H-rich BD4) and f is the final value. This result is in good agreement with a theoretical α value of 0.761 obtained by combining the $\alpha_{hornblende\text{-}water}$ [17] and $\alpha_{water\text{-}H2}$ [18] values at 800 ℃. Rayleigh fractionation curves using the theoretical $\alpha_{hornblende\text{-}H2\,(g)}$ values for 700-900 ℃ encompass most of the data for the slowly cooled kaersutites (Fig. 1), consistent with temperatures derived by experimentally dehydrogenating Ti-rich amphiboles [11-12]. Together, the results for our heat-treated and natural samples strongly support the interpretation that dehydrogenation processes influence the δD and H of Ti-rich amphiboles.

Implications for Mars: On the basis of small-scale, combined δD-H values, it is clear that dehydrogenation (equation 1) is an important process in natural kaersutites and may explain much of the δD variations in martian kaersutites. However, dehydrogenation alone cannot produce the extremely high δD observed in martian minerals (e.g., apatite), indicating that Mars has an intrinsically higher δD than Earth. Shock processes may induce additional heterogeneities that may complicate the effects of dehydrogenation [cf. 8].
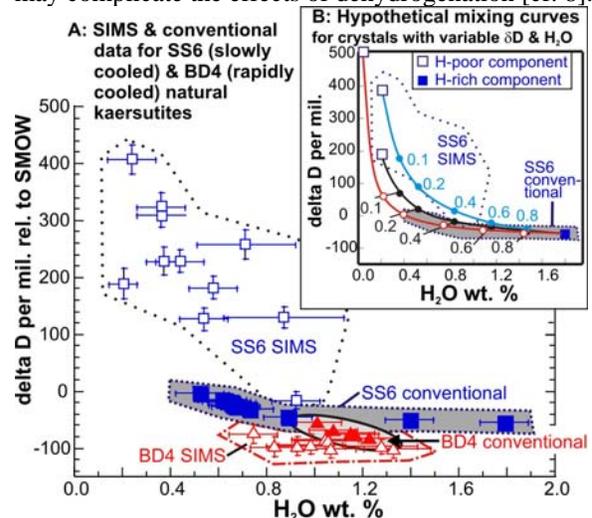

Fig. 2A: SIMS and conventional δD vs. H_2O for BD4 and SS6. **Fig. 2B:** Hypothetical mixing curves between H-poor and H-rich components in a heterogeneous crystal; in reality a range of components could be chosen. Curves were calculated using: $H_2O_{mix}=F(H_2O_A-H_2O_B)+ H_2O_B$ and $\delta D_{mix} = \delta D_A*[H_2O_A*F/H_2O_{mix}] + \delta D_B*[H_2O_B*(1-F)/H_2O_{mix}]$. The conventional δD-$H_2O$ analysis of a heterogeneous crystal is biased towards the H-rich component.

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