

HYDROGEN ISOTOPE MEASUREMENTS OF GYPSUM AND JAROSITE IN MARTIAN METEORITE ROBERTS MASSIF 04262: ANTARCTIC AND HOUSTONIAN WEATHERING. J. P. Greenwood¹ and S. Itoh², N. Sakamoto³, H. Yurimoto^{2,3} ¹Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT, USA (jgreenwood@wesleyan.edu), ²Dept. of Natural History Sciences, Hokkaido University, Sapporo, Japan, ³Creative Research Initiative "Sousei", Hokkaido University, Sapporo, Japan.

Introduction: The secondary minerals of Martian meteorites have long fascinated the scientific community due to their possible formation on Mars, which in turn can provide insight into weathering processes on Mars. Minerals such as jarosite have a restricted set of formation conditions and can provide information as to the pH, Eh, latitude and temperature of fluids on Earth [1-4]. Ca-sulfate (gypsum and/or bassanite) was first described in basaltic shergottite EETA 79001 [5]. Ca-sulfate, Ca-carbonate and Mg-phosphate salts in vugs show evidence of Martian origin from carbon isotopes of carbonate [6]. Jarosite has been recently described in the nakhlite MIL 03346 and has a Martian δD [7]. The findings of jarosite by MER at Meridiani Planum [8] and gypsum (and possibly bassanite) in Valles Marineris by the ESA MEX OMEGA [9] demonstrate the importance of these minerals as weathering products on the Martian surface. Terrestrial formation of these low-temperature alteration products is can provide valuable information, as constraints can be provided into how Martian basalts weather, although under different conditions.

While jarosite and gypsum/bassanite have been described from different classes of Martian meteorites, in the Roberts Massif 04262 shergottite, both minerals have been putatively identified [10]. Mineralogy and geochemistry of jarosite and gypsum analyzed here was described in [10]. Briefly, Fe-sulfide (pyrrhotite) and apatite show evidence of significant low-temperature alteration relative to that previously described in other shergottites and nakhlites [1,7,10]. A hydrous iron-phosphate is also associated with the jarosite mineralization. Here we report hydrogen isotope measurements of gypsum and jarosite in RBT 04262 in order to determine the last location of hydrogen isotope equilibration.

Methods: The Cameca ims 1270 ion microscope with SCAPS 2-D ion imaging detector at Hokkaido University (Hokudai) was used to determine the spatial variability and ratios of hydrogen and deuterium in gypsum and jarosite mineralization in RBT 04262,40. More detailed methodology can be found in [10], albeit modified for different mineralogy. Terrestrial jarosite and gypsum were used to correct for instrumental mass fractionation.

Results and Discussion: Two ion microprobe spot analyses of jarosite gave a δD of $-488 \pm 49\%$ and $-476 \pm 50\%$ (1σ). One ion probe spot analysis of gypsum was significantly different with a δD of $-21 \pm 14\%$ (1σ).

The area of interest for the jarosite work is shown in Fig. 1a. In Fig. 1b is the 1H ion image and the δD image in Fig. 1c. Cracks show up with high hydrogen in Fig. 1b. The similarity of δD in the jarosite mineralization area is important as the jarosite is intimately mixed with a hydrous iron phosphate (Fig. 1d), thus obtaining jarosite-only areas for isotopic analyses was extremely challenging. The similarity in δD suggests that the hydrous iron phosphate has a similar δD to the jarosite.

Jarosite. The hydrogen isotopes of jarosite can record the hydrogen isotope composition of their formation water. Equilibrium hydrogen isotope fractionation of jarosite-water has a δD of $-50 \pm 12\%$ at low temperatures [1]. Thus, jarosite in RBT 04262 last equilibrated with water with a δD of -438% to -426% . This hydrogen isotope value for water is indistinguishable from SLAP (Standard Light Antarctic Precipitation), which has a δD of -428% . These were difficult measurements with a large error bar, so the exact fit is probably somewhat fortuitous, but clearly an Antarctic origin for jarosite is the best explanation. Formation on Mars from mantle or crustal fluids would seem unlikely to produce jarosite with such a light hydrogen isotope value. Exchange rates of hydrogen isotopes in sulfates are poorly known, thus we cannot rule out formation of jarosite originally on Mars and then re-equilibration of hydrogen isotopes with antarctic waters during the meteorite's residence in Antarctica.

Gypsum. Hydrogen isotope value of gypsum in RBT 04262 is very different than that of jarosite. As with jarosite, the hydrogen isotope composition of gypsum can determine composition of water that the mineral last equilibrated with. The equilibrium hydrogen isotope fractionation factor for gypsum-water is -15% [11]. The water that gypsum in RBT 04262 last equilibrated with had a δD of $\sim -6\%$. This δD is inconsistent with equilibration with Antarctic water. It is more consistent with equilibration with water from a temperate latitude on the Earth [3]. The δD of spring-time water vapor in the Houston area is in the range of

-6‰ [12]. Thus, we propose that the gypsum in RBT 04262 last equilibrated with water in the curatorial facility in Houston, Texas. Again, the exchange rates of hydrogen isotopes in this phase are poorly known, thus we cannot rule out formation of this gypsum on Mars or Antarctica with later equilibration in Houston.

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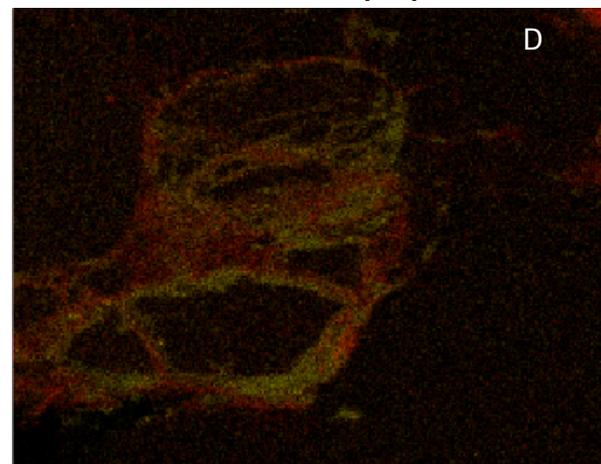
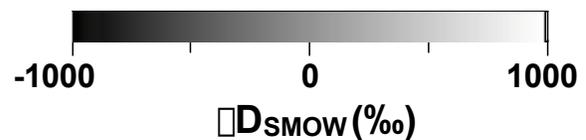
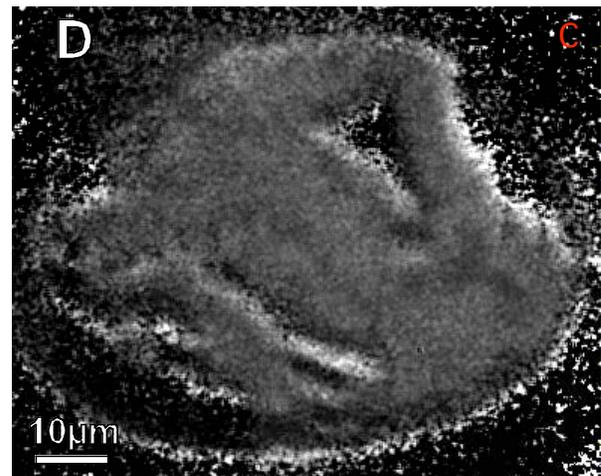
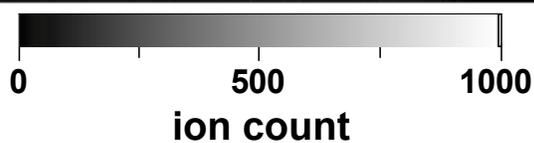
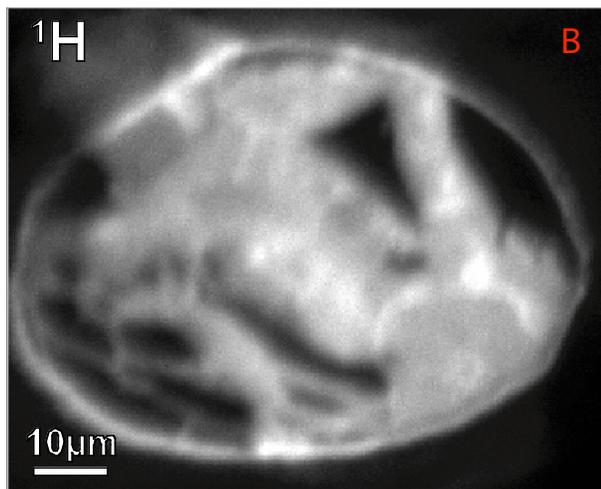
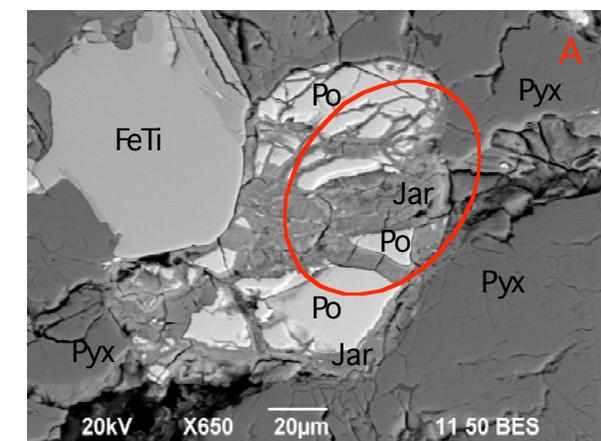


Figure 1. Images of jarosite mineralization area in RBT04262,40. (A) BSE image of jarosite mineralization in altered pyrrhotite. Red ellipse is the location of the SCAPS analysis shown in (B) and (C). The images in (B) and (C) are tilted approx. 120° clockwise to match up with the orientation shown in (A). Jar: jarosite; Po: pyrrhotite; Pyx: pyroxene; FeTi: Fe-Ti oxide. (B) ^1H image of jarosite mineralization. Cracks have higher hydrogen. (C) δD image of jarosite mineralization. Jarosite is intergrown with a hydrous iron phosphate; this image shows that the jarosite and hydrous iron-phosphate are similar in hydrogen isotope composition, shown in (D) $\text{K}\alpha$ x-ray maps of K (yellow) and P (red) of area in (A).