

HYDROGEN ISOTOPIC COMPOSITION OF THE WATER IN CR CHONDRITES. L. Bonal^{1,2,*}, C.M.O'D. Alexander¹, G.R. Huss², and K. Nagashima², ¹DTM, Carnegie Institution of Washington, Washington DC 20015, USA; ²HIGP/SOEST, University of Hawai'i at Mānoa, Honolulu, HI 96822, USA. *lbonal@ciw.edu

Introduction: Aqueously altered chondrites are composed of two main hydrogen (H) bearing phases: organics and hydrated minerals. Phyllosilicates and silicates in some aqueously meteorites are enriched in deuterium (D) relative to SMOW [e.g., 1,2], but the enrichments are smaller than in the respective organics [3]. An interstellar origin was attributed to the asteroidal water based on its D enrichment [1,2]. However, alternative hypotheses need to be tested. For instance, were the D enrichments in water inherited from the molecular cloud or nebula, or do they represent a later signature produced through secondary reprocessing?

Isotopic exchange between water and organics might have occurred during aqueous alteration. Indeed, it has been shown experimentally that isotopic exchange between water and organics is rapid at relatively low temperatures (comparable with those considered for CR chondrites). The exchange of H and D is not kinetically inhibited, and the extent depends on the intensity of the aqueous alteration process [4,5]. The size of the isotopic shifts depends on the isotopic compositions and relative abundances of the two reservoirs. Water on chondritic parent bodies could also have been isotopically fractionated and become more D-enriched through oxidation of Fe (in metal, sulfides, and silicates) and dehydrogenation of the organics [6]. Extrapolation of laboratory experiments, if they exist, to geological conditions always involves a degree of uncertainty. Nevertheless, it seems possible that the isotopic compositions of both water and organics may have been modified in the chondrite parent bodies during aqueous alteration.

The H isotopic compositions of water in various chondrites have previously been estimated by subtracting H in insoluble organics (IOM) from published bulk H data [6]. These estimates are informative but, due to several uncertainties (IOM abundances, soluble organics neglected, etc.), they do not provide a precise tool for addressing key questions about the origin and evolution of chondritic water. We thus set out to determine *in situ* the H isotopic compositions of hydrous silicates in primitive chondrites. Hydrated minerals are products of the aqueous alteration and their H isotopic compositions reflect those of the water that was present at the time they formed. By selecting a suite of CR chondrites that experienced different degrees of aqueous alteration (and escaped significant thermal metamorphism), and determining the isotopic composition of the water in different hydrated minerals, we hope to

place new constraints on the composition, evolution, and origin of asteroidal water.

Samples: MET 00426 and QUE 99177 are highly pristine CR chondrites that have experienced only incipient aqueous alteration [7]. EET 92042 and GRA 95229 have experienced higher degrees of aqueous alteration. Renazzo and Al Rais, both falls, are the most altered samples of our sample suite. The insoluble organic matter in all of these chondrites is highly D-enriched with $2600 \leq \delta D (\text{‰}) \leq 3100$ [3].

Analytical procedures: Preliminary characterization of the matrix areas and determination of the elemental compositions of hydrated silicates were carried out by SEM and EPMA, both at the University of Hawai'i (UH) and Department of Terrestrial Magnetism, Carnegie Institution of Washington (DTM).

H isotopic measurements: In order to avoid analytical artifacts (e.g., potential contamination by D-rich organics), but also to study the potential isotopic evolution of the water during alteration, we measured the H isotopic composition of (i) phyllosilicate-enriched fine-grained matrices, (ii) chlorite-type hydrated silicates, and (iii) altered chondrule glass. Initial measurements on phyllosilicates were carried out with the UH Cameca ims 1280 ion microprobe. Subsequent measurements were performed with the DTM Cameca ims 6f ion microprobe. To minimize the amount of adsorbed water on the samples, the sections were stored prior to analysis under vacuum in an oven at 50°C for several days. Terrestrial serpentines with known H isotopic compositions [8] were used to correct the instrumental isotopic mass fractionation.

Fine-grained matrix: the detailed analytical protocol used to measure the H isotopic composition of the phyllosilicate-enriched fine-grained matrix has been previously described by [9]. Because of their different ionization efficiencies, the H isotopic compositions of phyllosilicates can be measured with an O⁻ primary beam in a mixture of phyllosilicates and organics [1].

Hydrated silicates: H isotopes in chlorite-type silicates were measured at DTM. First, a 1-2nA Cs⁺ primary ion beam was rastered over a 10×10 μm² area for 180s. The data were then collected using a 0.25nA beam focused to 5-10μm in diameter. The normal-incidence electron gun was used for charge compensation. A field aperture was used to reduce the H ion contribution from areas beyond the crater rim. The mass-resolving power of the mass spectrometer was set to ~400. Negatively charged ions were counted (1s on H, ¹²C, and ³⁰Si, 15s on D) on an electron multiplier.

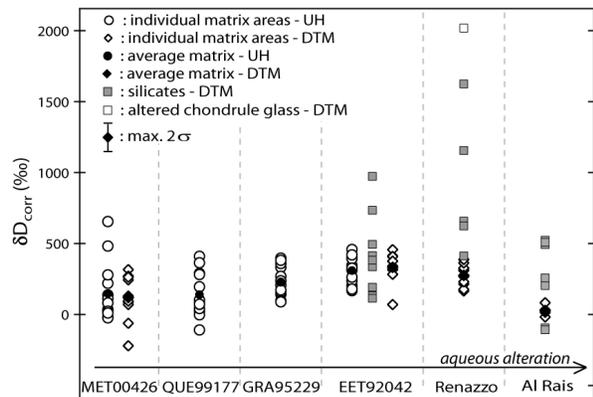


Fig. 1: D-enrichments of the phyllosilicate-enriched matrix and chlorite-type silicates for each considered CR chondrite.

Results: The corrected D/H ratios of phyllosilicate-enriched matrices, chlorite-type silicates, and altered chondrules glass are reported in δ -notation (‰) relative to SMOW for each studied CR chondrite in Fig. 1. Several observations can be made: (i) comparable D-enrichments were measured with the UH 1280 and DTM 6f ion microprobes for the matrices of MET 00426 and EET 92042; (ii) systematic D enrichments were observed in the matrix of each chondrite with the exception of Al Rais; (iii) systematic D enrichments were observed in the chlorite-type silicates; (iv) chlorite-type silicates are systematically more D-enriched than the matrix areas in Renazzo and Al Rais; (v) the altered chondrule glass is the most D-enriched phase measured in Renazzo; (vi) D enrichments in phyllosilicate-enriched matrices and chlorite-type silicates vary at the scale of our measurements in each sample.

Discussion: Terrestrial water could have exchanged with the hydrous mineral phases during residence of the meteorites in Antarctic (finds) and/or in the laboratory (finds, falls). The present measurements show that this exchange has not been pervasive enough to completely erase the D enrichments. Nevertheless, the present data might only provide lower limits on the true isotopic compositions of the water in the studied CR chondrites. Moreover, the phyllosilicates, present in the fine-grained matrix, potentially exchanged more with terrestrial water, during section making for instance, than the coarser-grained hydrated silicates. This could explain why: (i) the matrix phyllosilicates in Al Rais are not D-enriched, although it is the CR chondrite with the most D-rich estimated water composition [6]; and (ii) the D-enrichments in matrix phyllosilicates are systematically lower than in chlorite-type silicates in Renazzo and Al Rais.

The H isotopic compositions of the hydrous minerals vary in each sample ($\sim 0 \leq \delta D_{\text{phyllo}} (\text{‰}) \leq \sim 500$). This could be explained by the presence of several reservoirs of liquid water with different isotopic signa-

tures circulating on the CR parent body. The hydrothermal alteration might not have been pervasive enough to homogenize the D/H ratios of these reservoirs. A large spread is also observed among the hydrated silicates in Renazzo and Al Rais. In particular in Renazzo, the glassy mesostasis of one chondrule is much more enriched ($\delta D \sim 2000\text{‰}$) than the peripheral chlorite-type silicates ($\delta D \sim 1000\text{-}1500\text{‰}$). This difference (if not due to exchange with terrestrial water), could reflect an evolution of the H isotopic composition of the water during alteration.

The studied CR chondrites experienced a wide range of aqueous alteration. Although the average D-enrichments measured in the phyllosilicate-enriched matrices tend to slightly increase from MET 00426 to Renazzo (Fig. 1), there is no obvious difference between the CR chondrites, in terms of the water D-enrichment as measured in the matrices. The elemental compositions of the chlorite-type silicates nevertheless evolve along a defined trend with an increasing degree of aqueous alteration. More isotopic measurements need to be carried out on these meteorites to investigate whether this is accompanied with a H isotopic evolution of the water as well.

Different processes might have modified the isotopic composition of asteroidal water. In particular, the extent of the isotopic exchange between the H reservoirs will depend on their relative sizes, with the prevailing condition that the time-temperature of alteration was adequate to initiate this exchange. At present, the fact that the isotopic variability does not simply scale with the degree of aqueous alteration in CR chondrites makes it difficult to infer what the pristine isotopic composition of CR parent body was. Moreover, Renazzo contains water with D-enrichments that exceed those measured in three comets ($\delta D \sim 1000\text{‰}$ [10]). As chondritic parent bodies have experienced secondary reprocessing that cometary bodies escaped, it seems unlikely that the more D-enriched asteroidal water is more “pristine” than in comets. The highly D-enriched water in Renazzo tends to indicate a different, possibly secondary, isotopic fractionation process, hence, most likely distinct origins for cometary and CR waters.

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