

SUB-ZERO ALTERATION IN AN ISOTOPICALLY HEAVY BRINE PRESERVED IN A PRISTINE H CHONDRITE XENOLITH. D. R. Frank¹, G. R. Huss¹, K. Nagashima¹, M. E. Zolensky², dfrank@hawaii.edu, ¹Hawai'i Institute of Geophysics and Planetology, Dept. of Earth Sciences, University of Hawai'i at Mānoa, ²ARES, NASA Johnson Space Center, Houston, TX.

Introduction: Brecciated H chondrites host a variety of xenoliths, including unshocked, phyllosilicate-rich carbonaceous chondrites (CCs) [1-2]. The brecciated H chondrite Zag (H3-6) is one of two chondrites to host macroscopic (1 - 5mm), xenolithic crystals of halite (NaCl) with aqueous fluid inclusions and organics [3-4]. A ~1cm CC xenolith in Zag (Zag clast) has mineralogy similar to CI chondrites, but it has a unique bulk oxygen isotopic composition among all meteorites ($\Delta^{17}\text{O} = 1.49 \pm 0.04 \text{‰}$, $\delta^{18}\text{O} = 22.38 \pm 0.17 \text{‰}$) [5-6]. The Zag clast encloses halite in its matrix, linking the coarse, matrix halite and the xenolith to the same parent object, suggested to be hydrovolcanically active [4]. Its bulk C and N contents are the highest among chondrites and bulk $\delta^{15}\text{N}$ is similar to CR chondrites and Bells [7]. Insoluble organic material (IOM) in the Zag clast has δD and $\delta^{15}\text{N}$ "hotspots", also similar to CR chondrites and Bells (C2-ung.) [6-7]. We provide further isotopic characterization of the Zag clast to constrain the formation temperature and origin of its primary and secondary components.

Samples and Methods: We performed secondary ion mass spectrometry (SIMS) with the UH ion microprobe on a ~2x3mm section of the Zag clast. Oxygen isotopes were measured in multi-collection mode for olivine, augite, dolomite (dol) and magnetite (mgt). Hydrogen isotopes and ^{12}C were measured at 21 spots in matrix using mono-collection mode with $^{16}\text{O}^-$ beam defocused to ~30 μm and a field aperture gating to collect signals only from ~4x4 μm area. EPMA was performed on olivine, augite, carbonates, sulfides, and matrix.

Results: The Zag clast has a matrix with intergrown serpentine and saponite, similar to CIs, but it is more saponite-rich. Pyrrhotite and pentlandite are both present. Carbonates measured with EPMA are all dolomite with 5-8 % siderite. Magnetite and dolomite form large (100 - 400 μm) clastic aggregates with subgrains up to 100 μm . SIMS measurements of matrix are shown in Fig. 1 as D/H vs. $^{12}\text{C}/\text{H}$, although we must caution that we have not yet estimated a relative sensitivity factor for C/H. Nevertheless, we do observe wide ranges of both D/H and $^{12}\text{C}/\text{H}$ in the matrix, likely due to variable concentrations of IOM and fine-grained carbonates. Primary $^{16}\text{O}^-$ ions ionize H in phyllo-silicates ~500x more efficiently than in IOM [8]. Our mean D/H composition of matrix ($\delta\text{D} =$

$357 \pm 70 \text{‰}$ (1σ stdev)) shows that phyllosilicates were in extreme isotopic disequilibrium with the IOM measured in the same section ($\delta\text{D} \sim 2000$) by [6-7]. Combining our δD measurement with the bulk $\delta^{15}\text{N}$ value from [7], the Zag clast is similar only to CR chondrites and Bells among known solar system materials (Fig. 2).

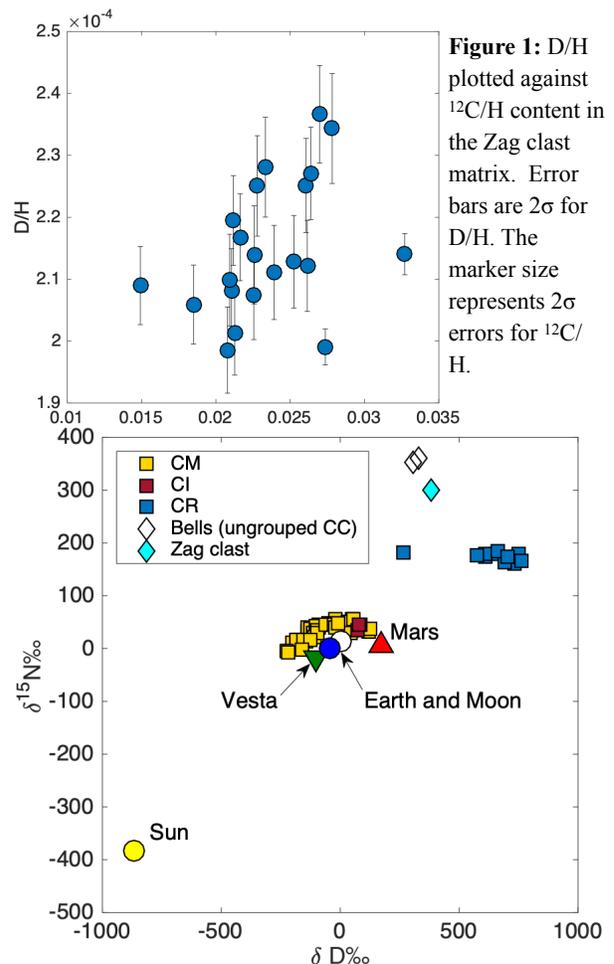


Figure 1: D/H plotted against $^{12}\text{C}/\text{H}$ content in the Zag clast matrix. Error bars are 2σ for D/H. The marker size represents 2σ errors for $^{12}\text{C}/\text{H}$.

Figure 2: Bulk δD [this work] and $\delta^{15}\text{N}$ [7] for the Zag clast compared to hydrous CCs [9], Earth, moon, Mars, Vesta, and the Sun.

Measurements of oxygen isotopes are shown in Fig. 3. Olivine and augite have O compositions that follow the PCM line, similar to CCs. Dolomite and magnetite are intergrown (Fig. 4), suggesting contemporaneous crystallization, and a weighted least

squares regression though their oxygen data gives a mass fractionation line with slope = 0.518 ± 0.007 and $\Delta^{17}\text{O} = 1.46$ ‰. We conclude that dolomite and magnetite were mass fractionated from the bulk composition in a closed system. $\delta^{18}\text{O}$ values for dolomite and magnetite clustered around +41 ‰ and -6 ‰, respectively, and oxygen isotope geothermometry gives a co-crystallization temperature $< -15^\circ\text{C}$. Slow kinetics of D-H exchange in a brine at sub-zero temperatures may explain the isotopic disequilibrium between organics and phyllosilicates, as indicated by experiments with deuterated IOM analogs [10].

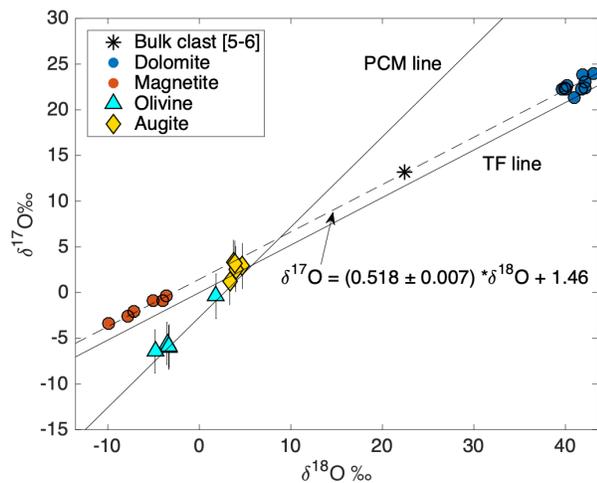


Figure 3: Oxygen isotopes in the Zag clast with weighted linear regression through dol and mgt. Note that the inferred $\Delta^{17}\text{O}$ value (1.46) for the precipitating fluid is in agreement with the bulk clast. 2σ errors are approximately the size of the markers unless shown.

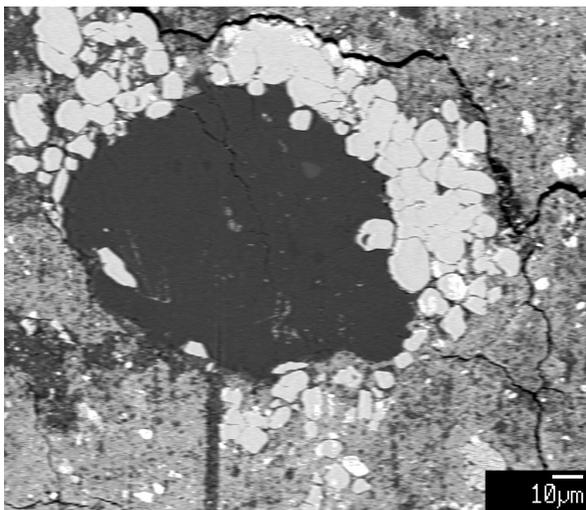


Figure 4: BSE image of several magnetite grains intergrown within and around dolomite.

Discussion: Because the Zag clast is associated with macroscopic, fluid-inclusion bearing halite, our -15°C temperature estimate indicates that aqueous alteration occurred in the presence of an icy brine. The δD and $\delta^{15}\text{N}$ hotspots in IOM from the Zag clast were preserved due to low temperatures in both the protosolar nebula and during aqueous alteration. Elevated δD in phyllosilicates indicates that either fluids incorporated interstellar ice [e.g., 8] or that D-poor H_2 was outgassed following oxidation of Fe metal [11]. Correlated bulk δD and $\delta^{15}\text{N}$ enrichments indicate that the clast's IOM experienced low-temperature ion-molecule reactions either in the interstellar medium or outer nebula. D/P type asteroids have been suggested as the source of the Zag clast [6-7].

CRs, Bells, and the parent object of the Zag clast form a group of chondritic materials with correlated δD and $\delta^{15}\text{N}$ enrichments (Fig. 2). The carrier of their $\delta^{15}\text{N}$ enrichments is IOM with H and N isotopic hotspots. Sources of bulk δD enrichments are IOM, interstellar water ice, and oxidation of Fe metal. We suggest that our minimum D/H measurements of the Zag clast matrix ($\delta\text{D} \sim 275$ ‰) estimate the fluid composition.

We are currently searching a 1kg sample of Zag for more xenoliths and are characterizing several C1 clasts in NWA 8369 (H5). The NWA 8369 xenoliths are saponite-rich with abundant magnetite, but they are carbonate-poor. δD and $\delta^{15}\text{N}$ measurements are pending. Xenoliths in brecciated H chondrites provide us with unique lithologies that are not available as meteorites, and may include suitable analogs for materials returned by asteroid sampling missions.

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References: [1] Rubin A. E. and Bottke W. F. (2009) *Meteoritics & Planet. Sci.* 44, 701-724. [2] Briani G. et al. (2012) *Meteoritics & Planet. Sci.* 47, 880-902. [3] Rubin A. E. et al. (2002) *Meteoritics & Planet. Sci.* 37, 125-141. [4] Chan Q. H. S. et al. (2018) *Science Adv.* 4, eaao3521. [5] Zolensky M. E. et al. (2003) *Meteoritics & Planet. Sci. Supp.* 38, A5216. [6] Kebukawa et al. (2019) *Nature Sci. Rep.* 9, 3169. [7] Kebukawa et al. (2020) *GCA in press*. [8] Deloule E. and Robert F. (1995) *GCA* 22, 4695-4706. [9] Alexander C. M. O'D. (2012) *Science* 337, 6095. [10] Kebukawa et al. (2014) *LPSC* 45, A1308. [11] Alexander C. M. O'D. (2010) *GCA* 74, 4417-4437.