

HYDROGEN CONTENT AND D/H OF CALCITE AS A POTENTIAL TRACER OF CARBONATE FORMATION IN CM CHONDRITES. M. Telus¹, M. Bose², and Z. Jin² ¹Earth and Planetary Sciences, University of California Santa Cruz, Santa Cruz, CA 95064 (mtelus@ucsc.edu), ²Center of Isotope Analysis, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287 (maitrayee.bose@asu.edu).

Introduction: Carbonaceous chondrites contain hydrated silicates, carbonates and oxides, all providing evidence of fluid-rock alteration in their parent bodies. Ca-carbonates are especially interesting because they precipitate directly from the fluid and can directly track changes in the composition of the fluid and conditions in the asteroid. Although carbonates such as calcite and dolomite are nominally anhydrous minerals, some hydrous and even amorphous Ca-carbonates, which are metastable, have been reported in terrestrial environments [1]. Given that, we do not completely understand what controls the formation conditions of carbonate grains in chondrite parent bodies, it is possible that hydrous and/or amorphous carbonates were precursors to the ones observed in chondrites. If so, a signature of the conditions can be expected in the hydrogen isotopic composition of the Ca-carbonate grains.

We have carried out preliminary hydrogen isotopic analyses of terrestrial carbonates (calcite and dolomite) and in a carbonaceous CM chondrite ALH 83100. Our preliminary data indicate that there is significantly more water in calcite in ALH 83100 than in our standards. The δD values of carbonates in the ALH 83100 are depleted, consistent with the bulk δD composition [2], and D/H analyses of phyllosilicates [3].

Samples: We analyzed calcite in a gold-coated thin section of CM ALH 83100. We analyzed terrestrial calcite and dolomite from the mineral collection at the University of California Santa Cruz. The terrestrial calcite and dolomite grains were mounted in Field's metal.

This meteorite has been studied extensively. Previous work on ALH 83100 includes in-situ carbon and oxygen isotopic analysis of calcite and dolomite [4], bulk D/H ratios [2], bulk carbon and oxygen isotope compositions of the carbonates [5], bulk chemical and petrographic analyses [6], and Mn-Cr age dating which indicate these grains formed a few million years after CAIs and not a product of terrestrial alteration [7].

NanoSIMS analyses: We carried out the hydrogen isotope analyses using the NanoSIMS 50L at Arizona State University. The sample and standards were coated with a conductive gold layer (~30 nm) prior to analysis. Approximately 48 hours prior to analysis, the samples were placed in the ultrahigh vacuum chambers of the NanoSIMS and allowed to achieve pressures between 8×10^{-11} to 1×10^{-10} Torr. We presputtered with a 580 pA of Cs⁺ current, followed by analysis with a 320 pA Cs⁺ beam (D1-3 in both cases). We measured ¹H⁻, ²D⁻, ¹²C⁻, and ¹⁸O⁻ simultaneously on electron multipliers.

We noticed that some of the grains were more hydrogen-rich than others, and was observed by the switching off of the trolley 1 electron multiplier measuring hydrogen. For these grains, we used a 20 pA of primary current for measurements. The primary ion beam was rastered over a $20 \times 20 \mu\text{m}^2$ area for presputtering and over a smaller $10 \times 10 \mu\text{m}^2$ area for analysis. Only 50% of the central region within this $10 \times 10 \mu\text{m}^2$ was measured via electronic gating to reduce the effects of adsorbed hydrogen. We presputtered for ~5 minutes while analyses were done for ~15 minutes (20 cycles). We used an electron gun with ~100 nA of current to compensate for sample charging. Analyses on cracks were excluded by monitoring the carbon intensities.

Results: Figure 1 shows the H counts for calcite in ALH 83100 and our standard. We observed that the hydrogen intensities is significantly higher (up to 3x higher) than that for the Ca-carbonate standards, indicating the water content of calcite in CM chondrites may be significant. We have not quantified the water contents yet and are in the process of acquiring bulk water contents of our standards. But qualitatively, the calcite in ALH 83100 is hydrated.

Figure 2 provides some examples of the cycle-to-cycle D/H values for Ca-carbonate standards and calcite in ALH 83100. Although some inter-grain variations are observed, the three calcite grains show very similar D/H ratios. Figure 3 shows the average D/H for standards versus calcite in ALH 83100.

Finally, the δD values for the calcite grains in ALH 83100 normalized to SMOW is shown in Figure 3. A majority of the measured spots have negative δD values, while 2 data points show δD values similar to the bulk δD values of this meteorite within uncertainties.

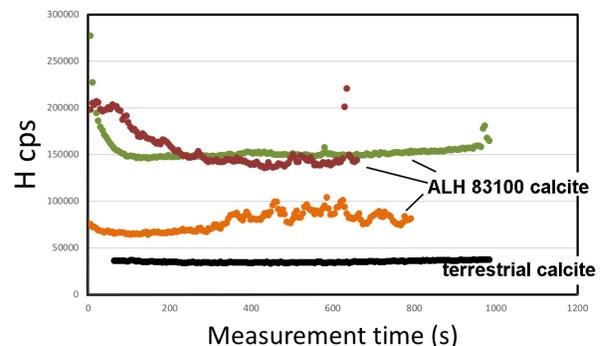


Figure 1. H content of terrestrial calcite (black) and calcite in ALH 83100 (red, green, orange).

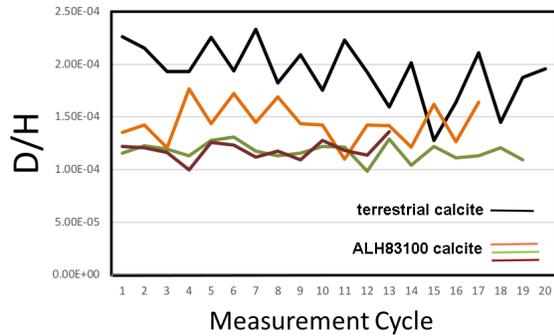


Figure 2. D/H of terrestrial calcite (black) and calcite in ALH 83100 (red, green, orange).

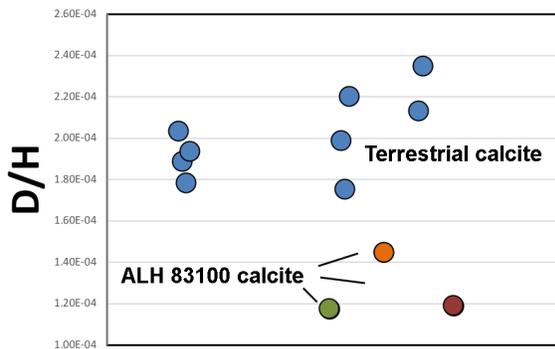


Figure 3. average D/H of terrestrial calcite (blue) and calcite in ALH 83100 (red, green, orange).

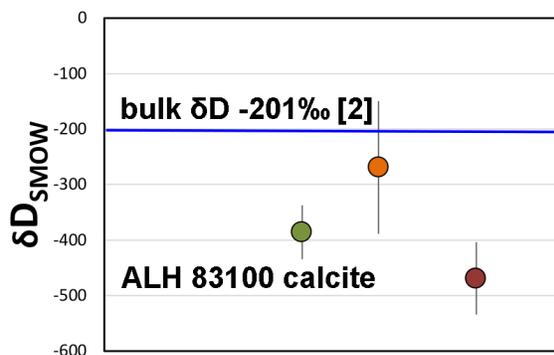


Figure 4. δD_{SMOW} of calcite grains in ALH 83100 and the bulk value determined by [2]. We do not know the bulk δD for our calcite standards, so these analyses were normalized to Standard Mean Ocean Water (SMOW). The errors are 2SE.

Discussion: D/H analyses of chondrites can be used to constrain whether chondrites formed in the inner solar system or the outer solar system, with the outer solar system planetesimals expected to be D-rich [7]. Our D/H analyses of calcite, which are thought to precipitate directly from the fluid, are consistent with D/H analyses of phyllosilicates [3] in carbonaceous chondrites that vary with some being depleted (-350‰) and others

being enriched ($>-69\text{‰}$). Our values are also consistent with bulk D/H analyses (-201‰) from [2].

Hydrogen content of calcite in ALH 83100 may be significant (Figure 1). We argue based on this preliminary assessment that the Ca-carbonate grains in ALH 83100 were initially hydrous. Ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) are metastable and tend to form as an intermediate phase to calcite and they are often associated with Ca-Mg-rich carbonates like dolomite [8], which are observed in highly altered CMs like ALH 83100 [4]. Water is bound to the carbonate ions in monohydrocalcite, which is stable under a wide range of conditions. Ikaite, on the other hand is only stable at temperatures below freezing [8]. The formation of hydrated calcite is highly sensitive to the Mg content of the fluid and is associated with water percolation through amorphous calcite [8-10].

The δD values are consistent with previous analyses [2, 3]; however, we have not accounted for instrumental mass fractionation adequately. We will determine the H content and δD values for our standards to better quantify the data on ALH 83100.

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References: [1] Zou Z. et al., 2019. *Science* 363, 396-400. [2] Alexander C. M. O'D. et al. 2013. *Geochim. Cosmochim. Acta*, 123, 244-260. [3] Piani L. et al. 2015. *Earth Planet. Sci. Lett.* 415, 154-164. [4] Telus M. et al., 2019. *Geochim. Cosmochim. Acta*, 260: 275-291 [5] Alexander C. M. O'D. et al. 2015. *Meteorit. Planet. Sci.*, 50: 810-833. [6] Zolensky M. E., et al. 1993. *Geochim. Cosmochim. Acta* 57, 3123-3148. [7] de Leuw S. et al. 2009. *Geochim. Cosmochim. Acta*, 73, 7433-7442. [#] Robert F. 2006. *MESSII*. 341-351. [8] Sekkal W. and Zaoui A. 2013. *Scientific Reports*. 3, 1587, DOI: 10.1038/srep01587. [9] Chaka A. M. 2019. *J. Phys. Chem. A* 2019, 123, 13, 2908-2923. [10] Rodriguez-Blanco J. D. et al., 2012. European Mineralogical Conference, 397, <https://meetingorganizer.copernicus.org/EMC2012/EMC2012-397.pdf>.