REVISITING THE ORIGIN OF CARBONATES IN ELEPHANT MORAINE A79001 AND POSSIBLE EVIDENCE FOR LIQUID WATER ON MARS IN THE AMAZONIAN. P. B. Niles[1], T. Sun[2], E.L. Berger[3], M.E. Evans[1], and M. El-Shenawy[4] [1]NASA Johnson Space Center, Houston, TX 77058 (paul.b.niles@nasa.gov),[2]Rice University, [3]Jacobs, NASA Johnson Space Center, Houston, TX 77058, [4]University Space Research Association, Johnson Space Center.

Introduction: Carbonate minerals of martian origin are present in several martian meteorites in trace concentrations (< 1%) and possess unique isotopic signatures that suggest that the martian environment and/or isotopic reservoirs are very different from the Earth's [1–3]. Carbonates are most common in the older martian meteorites (Allan Hills 84001 and the nakhlites), however, there have been reports of carbonate in the younger shergottites including Elephant Moraine A79001 [1,4]. Acidification studies of Zagami and Shergotty have shown that CO_2 is released suggesting that carbonate phases are present in these meteorites [4], but the origin of these phases is controversial.

The young ages of the shergottites [5] makes them important samples for understanding the modern martian environment. The carbonates in EETA 79001 are the best-characterized secondary minerals in a shergottite, but their origin remains controversial. Gooding et al. [1] argued that two types of carbonate occur within the glassy parts of the meteorite. One type, nearly pure $CaCO_3$ associated with Ca-sulfate shows textural evidence for being present in the rock prior to it being shocked, suggesting formation on Mars. The second was more abundant and consists of Ca-rich carbonate, possibly with finely intergrown Mg-phosphate, but does not possess any textural relationships indicative of a martian origin. Carbon and oxygen isotopic studies of this carbonate yielded oxygen isotopes that potentially suggest a martian origin as well [6, 7] (Fig 1).

Are Elephant Moraine A79001 Carbonates Terrestrial? Many of the ordinary chondrites collected in Antarctica exhibit some form of weathering, and studies have shown that carbonates are a typical weathering product [8, 9]. Velbel et al. [9] suggest that at least 5% ordinary chondrites collected in Antarctica show visible white crusts, while spectroscopic measurements suggest that this weathering may be ubiquitous [10]. The most well studied example of Antarctic carbonate formation would be LEW 85320 which has been shown to contain hydrated Mg-carbonate with an isotopic composition consistent with formation from terrestrial reservoirs [11]. In addition, the ^{14}C signature of this carbonate weathering product suggests formation in the past 40 years [11].

Indigenous carbonate is rare in ordinary chondrites of higher petrologic type (types 4-6) which therefore can serve as reliable witness plates for Antarctic weathering processes.

A few studies have analyzed the isotopic composition of carbonates in Antarctic ordinary chondrites [12, 13]. The carbonate analyses have focused primarily on meteorites recovered from the Allan Hills region with a few exceptions. When compared with data from the martian meteorites (Fig. 1) a number of interesting observations can be made raising some unanswered questions.

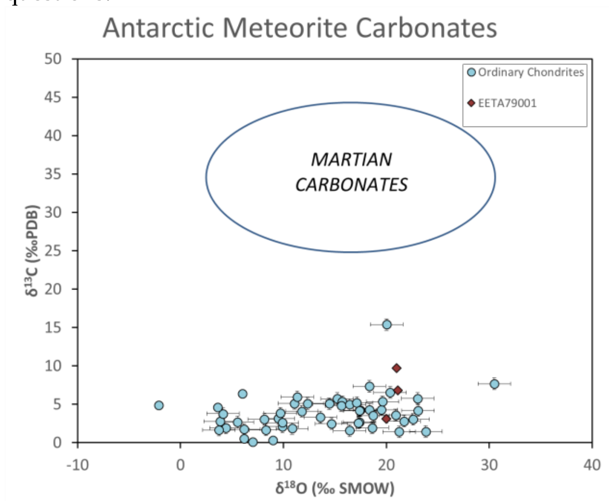

Figure 1. Measurements of carbonates in Antarctic ordinary chondrites (petrologic type 4-6) [14,15] compared to measurements of carbonates in EETA 79001 [6], [7].

Terrestrial weathering phases in ordinary chondrites (blue circles in Figure 1) describe a fairly clear field with $\delta^{13}C$ values varying between 0‰ and +10‰ but $\delta^{18}O$ values varying over a larger range between -5‰ and +30‰. The carbon isotopes are consistent with forming from an atmospheric source, but some of the EETA 79001 analyses may show mixing with a source more enriched in ^{13}C. The large range in oxygen isotopes is more difficult to interpret especially since carbonate in equilibrium with Antarctic meltwater should have a $\delta^{18}O$ value much less than 0‰ [6]. In addition, Evans et al. [13] showed a clear distinction in $\delta^{18}O$ between Ca-rich carbonates which have higher $\delta^{18}O$ values and Mg-, Fe-rich carbonates which have lower $\delta^{18}O$ values for reasons that are unclear.

Finally Jull et al. [14] performed several acidifications of portions of EETA 79001 and measured large ^{14}C concentrations suggesting that the carbonates in EETA 79001 are largely from Antarctic weathering. Jull et al. [14] also noted that the stable isotope compositions were very similar to carbonates from ordinary chondrites (Fig. 1).

This study seeks to separate the terrestrial weathering products from the indigenous carbonate through a careful, coordinated analysis program combining state of the art FIB/TEM/NanoSIMS studies with high precision multi-isotope analyses of stepped extractions.

Methods: A small ~100 mg chip from the interior of EETA 79001 was gently crushed to expose fracture surfaces. Several smaller pieces were mounted and coated with platinum for Scanning Electron Microscope imaging (SEM). One carbonate deposit identified during SEM imaging (Fig 2) was selected for Focused Ion Beam (FIB)-SEM sampling (Fig 2), and the resulting FIB section was analyzed on a Transmission Electron Microscope (TEM) at Johnson Space Center.

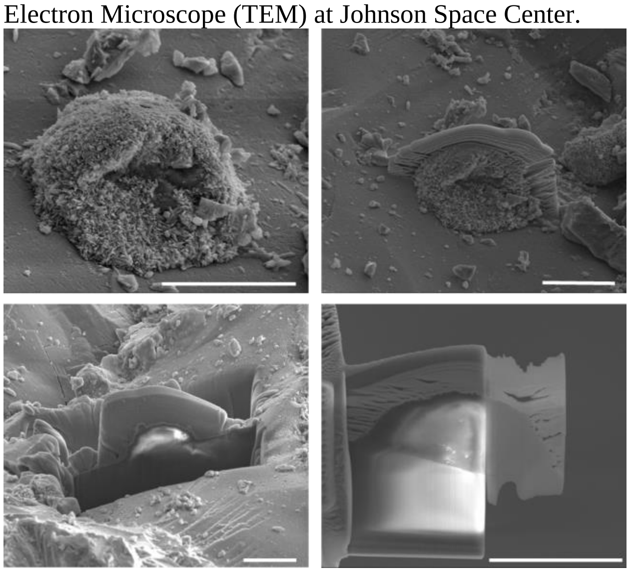

Figure 2. FIB-SEM sectioning of carbonate from EETA 79001. A protective platinum cap was placed over the region of interest, and material surrounding the region was milled out. Final FIB section at lower right contains a thinned region for TEM analysis on right and a thick (bright) section for future NanoSIMS analysis. White scale bars are 10 µm.

Results and Discussion: The carbonate region identified in EETA 79001 showed extremely fine nanoscale crystalline structure (Fig 3). Measurements from selected area electron diffraction patterns and EDS spectral data were used to identify the carbonate grains as aragonite. The deposit resembled carbonate clusters identified in Gooding et al. [1]) that showed common "massive, structureless" carbonates. The crystals detected were relatively pure $CaCO_3$ and contained no detectable impurities. The carbonate region sampled here is not the only type of carbonate found in the meteorite but is perhaps the most common [1].

Aragonite formation is not common at colder temperatures on Earth, but can form in solutions with Mg : Ca ratio of 4:1 or higher [15]. These conditions are consistent with what might be expected on Amazonian Mars, however it is unclear if aragonite formation is a common Antarctic weathering product. Direct comparisons with carbonates formed in ordinary chondrites (now underway) as well as upcoming NanoSIMS analyses should provide much needed insight into the origin of these carbonates.

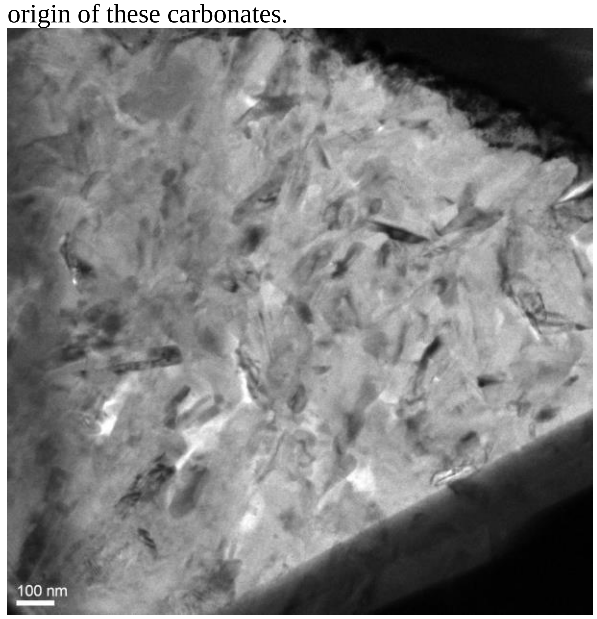

Figure 3. TEM image of nanocrystalline texture of EETA 79001 carbonate.

References:

[1] J. L. Gooding, S. J. Wentworth, and M. E. Zolensky, *Geochim. Cosmochim. Acta*, vol. 52, no. 4, pp. 909–915, 1988. [2] A. J. T. Jull, C. J. Eastoe, S. Xue, and G. F. Herzog, *Meteoritics*, vol. 30, no. 3, pp. 311–318, May 1995. [3] C. S. Romanek *et al.*, *Nature*, vol. 372, no. 6507, p. 655, Dec. 1994. [4] M. M. Grady, I. P. Wright, and C. T. Pillinger, *J. Geophys. Res. Planets*, vol. 102, no. E4, pp. 9165–9173, Apr. 1997. [5] L. E. Nyquist, D. D. Bogard, C.-Y. Shih, A. Greshake, D. Stöffler, and O. Eugster, *Space Sci. Rev.*, vol. 96, no. 1–4, pp. 105–164, Apr. 2001. [6] R. N. Clayton and T. K. Mayeda, *Geochim. Cosmochim. Acta*, vol. 52, no. 4, pp. 925–927, Apr. 1988. [7] I. P. Wright, M. M. Grady, and C. T. Pillinger, *Geochim. Cosmochim. Acta*, vol. 52, no. 4, pp. 917–924, Apr. 1988. [8] M. A. Velbel, *Meteoritics*, pp. 151–159, Jun. 1988. [9] M. A. Velbel, D. T. Long, and J. L. Gooding, *Geochim. Cosmochim. Acta*, vol. 55, no. 1, pp. 67–76, 1991. [10] M. Miyamoto, *Earth Planet. Sci. Lett.*, vol. 96, no. 1–2, pp. 229–234, 1989. [11] A. J. T. Jull, S. Cheng, J. L. Gooding, and M. A. Velbel, *Science*, vol. 242, no. 4877, pp. 417–419, 1988. [12] M. M. Grady, I. P. Wright, P. K. Swart, and C. T. Pillinger, *Geochim. Cosmochim. Acta*, vol. 52, no. 12, pp. 2855–2866, Dec. 1988. [13] M. E. Evans, P. B. Niles, D. R. Locke, and P. Chapman, Lunar and Planetary Science Conference, 2017, vol. 48, p. 2727. [14] A. J. T. Jull *et al.*, Lunar and Planetary Science Conference, 1992, vol. 23. [15] J. W. Morse, Q. Wang, and M. Y. Tsio, *Geology*, vol. 25, no. 1, pp. 85–87, Jan. 1997.