

**DOLOMITES IN HYDRATED FINE-GRAINED ANTARCTIC MICROMETEORITES: EFFECTIVE TOOLS FOR ANALYZING ALTERATION CONDITION.** E. Dobrică<sup>1</sup>, C. Engrand<sup>2</sup>, and K. K. Ohtaki<sup>1</sup>, <sup>1</sup>Hawai'i Institute of Geophysics and Planetology, School of Ocean, Earth Science, and Technology, University of Hawai'i at Mānoa, Honolulu, Hawaii 96822 USA. [dobrica@hawaii.edu](mailto:dobrica@hawaii.edu). <sup>2</sup>IJCLab, CNRS/IN2P3 Université Paris-Saclay, 91405 Orsay Campus, France.

**Introduction:** Carbonates are excellent candidates to study the secondary processes that modified the primitive materials that formed in the Solar System. They have the potential to provide us a high fidelity record of environmental conditions and the timing of their formation. Furthermore, they have been commonly identified in carbonaceous chondrites (<2 vol%), though they are rare in dust particles [1-6]. Recently, centimeters-thick, roughly meterlong veins of carbonates were identified in outcrops at the surface of the asteroid Bennu [7]. Here we expand on earlier efforts to investigate the secondary processes and the alteration conditions of hydrated fine-grained Antarctic micrometeorites (H-FgMMs), with a focus on the carbonates. We use site-specific extraction techniques to investigate the mineralogy, texture, chemical compositions of several electron transparent sections of one of the micrometeorites described previously only by oxygen isotopic measurements [1].

**Sample and methods:** One unmelted H-FgMMs (03-36-46) was analyzed in this study using extensive TEM techniques. The sample was collected from the pristine Concordia snow during the 2002 campaign [8]. The size of the particle analyzed in this study is 43 x 112 µm, which corresponds to the whole particle collected from snow. The polished and carbon-coated petrographic section was first characterized by scanning electron microscopy (SEM) using backscattered electron imaging on a Helios 660 dual-beam focused ion beam SEM (FIB-SEM) instrument at the Advanced Electron Microscopy Center (AEMC) at UH Mānoa. Four electron transparent sections were prepared by the conventional *in situ* FIB technique. A platinum protective layer was deposited on top of the region of interest, first by electron beam deposition and then by ion beam deposition, to avoid gallium primary ion beam damage during the FIB sample preparation. The section was transferred to Cu transmission electron microscopy (TEM) half grids with a micromanipulator. The final ion milling of the 2 µm thick section to electron transparency was carried out with the sample attached to the TEM grid. The final thinning stages were performed at 2 kV with a current of 72 pA. Each FIB

section was studied using a variety of TEM techniques, including scanning transmission electron microscopy (STEM) imaging, nanodiffraction, and energy-dispersive X-ray spectroscopy (EDS). All imaging and analysis were carried out at 300 kV using the Titan G2 analytical (S)TEM at AEMC. Crystalline phases were identified by electron nanodiffraction and EDS. Nanodiffraction was carried out with an accelerating voltage of 300 kV, a camera length of 295 mm, and a convergence angle of 0.1–0.3 mrad.

**Results:** Nonstoichiometric, Ca-rich dolomite grains  $[\text{Ca}_{0.9-1}\text{Fe}^{2+}_{0.1-0.2}\text{Mg}_{0.8-0.9}\text{Mn}^{2+}_{0.1-0.2}(\text{CO}_3)_2]$  were identified in two different FIB sections (1.0-1.2 Ca/Mg). All grains contain large concentrations of manganese and iron (N = 4, avg. 8.7 wt% MnO, 5.9 wt% FeO). They occur both as separate, anhedral, single crystals and as polycrystalline grains (Fig. 1). The size of the dolomite crystals varies in size from 900 nm to 3.5 µm. These dolomite grains show fine microstructural features called modulations, which appear as near-parallel lamellae or domains with regular, alternating dark/light contrast. Figure 1b shows these features that were emphasized using a high convergence angle of 0.1–0.3 mrad in the STEM mode. The modulations affect the entire crystal and show multiple orientations.

In the AMM analyzed the dolomite grains are associated with amorphous materials (white arrows, Fig. 1) with peculiar compositions such as high concentrations in manganese (up to 15.7 wt% MnO), sodium (36.4 wt% Na<sub>2</sub>O, Fig. 1c), sulfur (21.1 wt% SO<sub>2</sub>), and phosphorus (6.2 wt% P<sub>2</sub>O<sub>5</sub>). Furthermore, a variety of secondary phases (phosphates, framboidal and radial magnetite, and phyllosilicates) and features (embayments in pyrrhotite, pores in the phosphates, pseudomorphic replacements of primary phases by fine-grained phyllosilicates) were observed in the FIB sections analyzed, indicating that this H-FgMMs was extensively altered (Fig. 1).

**Discussion:** Dolomite was previously identified in CI, CM, and CR2 chondrites and AMMs [5-6, 9]. However, the dolomite grains identified in this study shows different chemical compositions and textures that the ones described previously. The manganese

abundance of these dolomite grains is twice as high (14.9 wt%  $\text{MnCO}_3$ ) compared to the one measured in CM chondrites [ $>6.9$  wt%  $\text{MnCO}_3$ , 5]. This enrichment, apart from cation concentration in the fluid, has important information about the redox potential of the pore fluids, which also controls the levels of Mn and Fe in the dolomite lattice. Previous studies indicate that the presence of both elements is favored by reducing conditions in the fluids [10-11]. The peculiar compositions of the amorphous materials associated with these dolomite grains may retain information about the chemical composition of the aqueous fluid from which the dolomite grains precipitated.

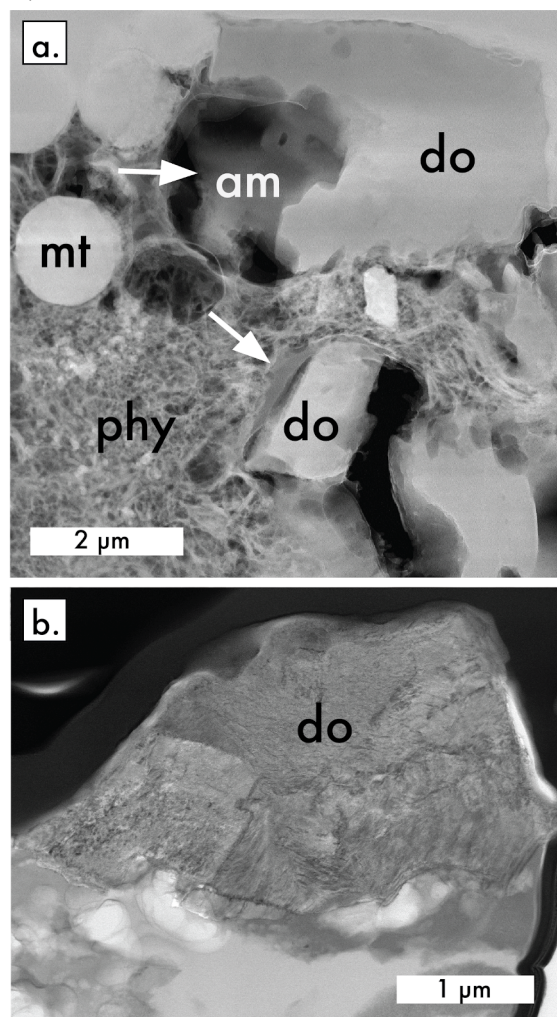
Additionally, the dolomite grains identified in this study show the presence of a fine-scale modulation microstructure [12-14]. Previous studies of terrestrial dolomites show that virtually all Ca-rich dolomites exhibit heterogeneous microstructures and fine modulations formed directly during crystal growth [13]. Detailed TEM work has also shown that the structural modulations appear to be oriented parallel to the growth direction of the crystals [12-14]. In adjacent growth sectors, the orientation of the modulation differs but remains consistent with growth direction. These fine microstructures form due to compositional heterogeneities and variation in fluid composition at the mineral-solution interface as lateral growth processes [12-14]. Additional EDS measurements are needed to understand if these fine microstructures are the result of a microcellular growth mechanism with an accumulation of impurities between the cells, as it was suggested by the analysis of terrestrial carbonates [14].

**Conclusion:** This study shows that the composition of fluids responsible for the alteration of this AMM have varied locally during dolomite growth and were enriched in Mn and Fe, indicating reducing conditions in the fluid. Further studies need to be carried out to fully assess the relationship between the heterogeneous fine-scale modulation microstructure, temperature of formation, composition, and reaction mechanism of dolomitization.

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**Figure 1.** a) Dark-field STEM image showing the association of dolomite (do) with amorphous materials (white arrows) and other secondary phases, such as phyllosilicates (phy) and magnetite (mt). b) Bright-field STEM image showing strong diffraction contrast of somewhat regular, alternating dark/light contrast in dolomite showing a fine-scale modulation microstructure.