

**MN CARBONATES IN THE MARTIAN METEORITE NAKHLA: POSSIBLE EVIDENCE OF BRINE EVAPORATION** J. V. Bailey<sup>1</sup>, D. S. McKay<sup>2</sup> and S. J. Wentworth<sup>3</sup>, <sup>1</sup>Dept. of Geosciences, Univ. of Arizona, Tucson AZ 85721-0077, jbailey@jupiter.lpl.arizona.edu, <sup>2</sup>NASA-Johnson Space Center, Houston, TX 77058, <sup>3</sup>Lockheed Martin, C23, 2400 NASA Rd.1, Houston, TX.

**Introduction:** The importance of secondary phases in martian meteorites lies in their potential to provide clues about the martian environments responsible for their formation. During this study, we analyzed a number of carbonate-bearing fracture surfaces from the Nakhla meteorite. Here we describe the physical and chemical properties of several manganese-calcium-rich siderites. Additionally, we describe a potential model for the formation and alteration of these carbonates, and we suggest constraints on the conditions responsible for their precipitation.

Nakhla is an olivine-bearing clinopyroxenite with minor amounts of feldspar, FeS, and Fe oxides. Secondary mineral assemblages include vein filling clays with embedded iron oxides, a calcium sulfate, amorphous silica, chlorapatite, halite and carbonates. Bridges and Grady [1] suggested that the carbonates in Nakhla formed from brine evaporation [2, 3]. Isotope studies of the Mn-rich siderite are also consistent with formation from hydrothermal fluids with an upper T constraint of ~170C[4].

**Experimental Methods:** Small (mm-sized) chips from the interior of the Nakhla meteorite were stub mounted using quickset epoxy. These chips were sputter coated with a 50Å coating of platinum prior to imaging and analysis using a JEOL 6340 field emission scanning electron microscope (FESEM). EDS analyses were performed using an IXRF energy dispersive X-ray spectroscopy (EDS) system operating at 15kV accelerating voltage.

**Carbonates and their micro-geological context:** Fe-rich carbonates in Nakhla constitute ~30-100 ppm of the rock [4]. Siderite in Nakhla was initially reported by [5], while small veins of calcium carbonate are mentioned by [6] and further characterized by [7]. Although the martian origin of carbonates and halites in Nakhla has not been firmly established, calcium sulfate, magnesium sulfate and secondary silicates have been shown to be pre-terrestrial by fusion crust disruption in grains near the meteorite's exterior [6,8]. The spatial association of both carbonates and halites with established pre-terrestrial phases suggests that these secondary alteration products are also pre-terrestrial.

The grains in our study were chips removed from areas containing preexisting fracture surfaces inside the Nakhla meteorite. The grains contain a variety of secondary alteration materials including clays, calcium sulfate, halite, and carbonates. The grain containing the carbonates is covered with numerous carbonate concretions which range in size from 100 µm to < 1 µm. The carbonates overlay an olivine or pyroxene substrate and rest within depressions. The olivine/pyroxene substrate surrounding the carbonate concretions is covered by a thin

silicate film, probably the mixture of phyllosilicates, Fe-oxides and amorphous material typical of secondary veins in Nakhla [9]. Numerous isolated euhedral calcium sulfate crystals sit atop, or are embedded in, this thin secondary silicate layer.

The carbonate concretions consist of foliated asymmetrical plates joined by thin protrusions (Fig. 1). Many of these stacks are offset by linear sub-parallel pits. The composition of these carbonates lies within the calcite-rhodochrosite-siderite ternary field for carbonates (Fig. 2).

While a "typical" point EDS shows a carbonate with nearly equal Fe, Mn, and Ca cation ratios, analysis of compositional abundances acquired from individual pixel spectra from elemental x-ray maps reveals compositional heterogeneity on a much smaller scale.

In many areas, the carbonate rest on top of a Cl, Fe-rich silicate film. In some places, this film exhibits a complex texture similar to that seen in the carbonates. Additionally, a possible relict cleavage or parting surface of the highly altered pyroxene or olivine is visible within the texture. Carbonate replacement of feldspars often follows cleavage or parting surfaces; however, the chemical composition of this base material is not consistent with a feldspar. Carbonate replacement of feldspar was suggested by [10] for the petrogenesis of the ALH84001 carbonates.

**Discussion:** The microstratigraphy of the Fe-Ca-Mn-carbonate is consistent with a precipitation model in which a low to moderate temperature hydrothermal system lays down a basal clay layer while creating a texturally complex framework of silicate alteration products by acting on parting or cleavage planes from the altered olivine or pyroxene substrate. This framework then serves as a nucleation surface for subsequent low temperature precipitation of carbonates from evaporation of a brine. Alternatively, differential dissolution acting on stratified carbonate laminae could produce a complex textural morphology.

The superposition of Ca and Mn carbonates over a siderite core is consistent with thermodynamic models of evaporation on early Mars under high P<sub>CO2</sub> conditions as presented by Catling [11]. The calcium sulfate crystals present elsewhere on this grain are an expected product of such a low temperature evaporation sequence and the sub-micron heterogeneity of the carbonates is also consistent with a low-temperature origin. Hydrothermal carbonate precipitation would likely homogenize chemical partitioning at this scale [12].

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While Ca, Ca-Mg, and even Fe carbonates are important sedimentary phases on Earth, Mn carbonates are less common. Under high temperature aqueous conditions, rhodochrosite, and its dolomitic counterpart, kutnohorite  $[\text{CaMn}(\text{CO}_3)_2]$ , are generally restricted to hydrothermal deposits. The atmospheric  $P_{\text{CO}_2}$  conditions of an early Martian atmosphere would have had a strong influence on the pH of surface aqueous environments, with significant ramifications for carbonate precipitation [11]. In addition to Eh, pH, pressure, and temperature, the cation concentration of the solution constrains the composition of the precipitated carbonate phase [13]. While manganese concentrations in both terrestrial freshwater and seawater are measured in  $\mu\text{g kg}^{-1}$  [14], the manganese concentration of anoxic hypolimnia in some lakes is measured in  $\text{mg kg}^{-1}$ . Among other factors, stratification of standing water, leaching from Mn-rich country rock, microbial activity, or cation partitioning during groundwater percolation could cause Mn to be supersaturated in solution. Siderite precipitating from such a solution under high  $P_{\text{CO}_2}$  has the potential to substitute Ca and Mn cations into its structure, potentially producing a solid solution similar to that seen in this study. The secondary mineral assemblage presented here lends support to the evaporite sequence predicted by Catling [11] for closed basin lakes on Mars. The secondary mineral assemblages in Nakhla described here and by others [1, 5, 6, 7] are consistent with low temperature precipitation from an evaporating brine, possibly following an earlier stage of mid-temperature hydrothermal activity. Such conditions could occur in a volcanic or impact-generated hydrothermal system with subsequent lacustrine brine development in the caldera or crater basin.

**Mn Carbonates as Indicators of Microbial Activity:** The possibilities for either biogenic or abiotic origins, or perhaps a combination of the two, need further investigation. On Earth, low-temperature Mn carbonate precipitation is often microbially mediated. Significant amounts of biotic manganous carbonate have been discovered in the Baltic Sea [14]. Additionally, bacterially precipitated rhodochrosite has been produced under laboratory conditions by *Geobacter metallireducens* [15]. Future studies using ion microprobe analysis of  $^{13}\text{C}/^{12}\text{C}$  and  $^{34}\text{S}/^{32}\text{S}$  may be able to differentiate between these two possibilities. Stable isotope fractionation on Earth can be used as an indicator of microbial activity because metabolic processes can lead to enrichment in the lighter isotopes of carbon and sulfur. The microscopic textures of the carbonates in this study also exhibit a complex morphology. The possibility that this texture could have been produced by either abiotic processes or through biological activity underscores the need to develop good criteria for identification of microbial precipitates.

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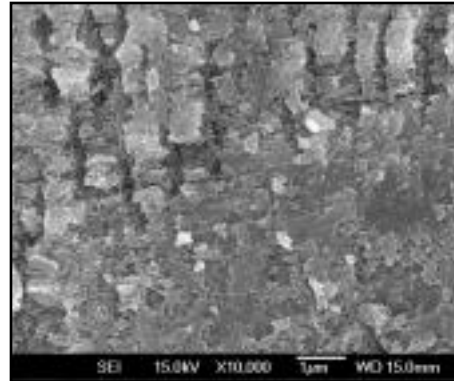


Figure 1. Nakhla carbonate texture. The topographically high areas (upper left) appear richer in Ca and Mn carbonate, while the low areas (lower right) appear to be enriched in Fe-rich carbonate. Backscatter images of the carbonate (not shown) show abrupt compositional changes over distances  $<100\text{nm}$ .

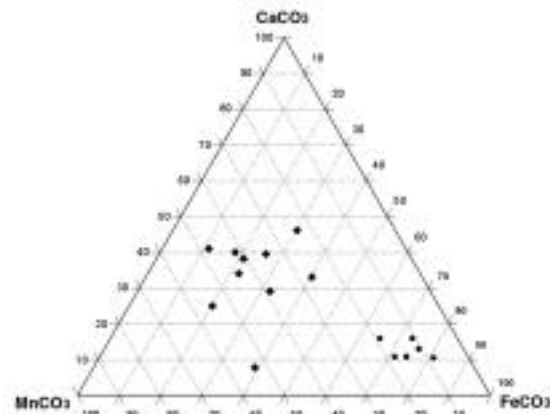


Figure 2. Ternary plot of semi-quantitative mole fractions acquired from EDS analysis of x-ray mapping. The  $\bullet$ s are from topographically low areas, while the  $\circ$ s represent analyses of topographically high areas.