MARTIAN AQUEOUS ALTERATIONS IN ALH 84001 AND THE NAKHLITE METEORITES.

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ALH 84001: Water-deposited minerals are present throughout ALH 84001 [1]. They formed deposited at ~3.9 Ga [2], and bear witness the chemical and physical conditions of an ancient aqueous system. These clues are partially obscured by shock effects [3], and their interpretation has been muddied by now-discredited claims of evidence for biological activity.

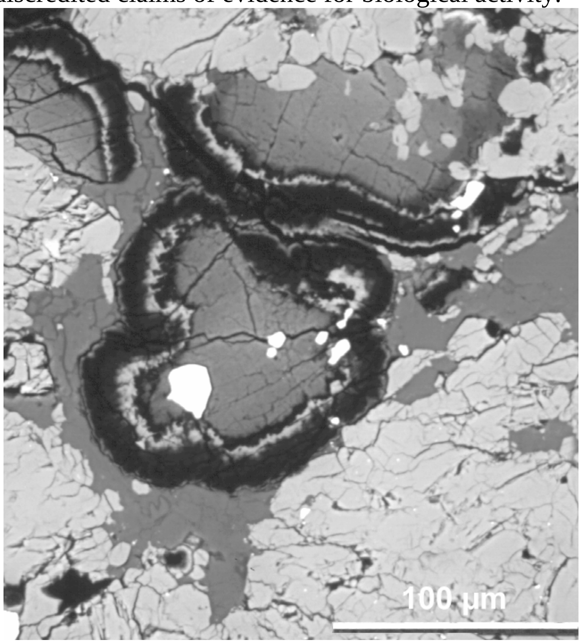

Figure 1. BSE thin section image [3] of carbonate globules (banded) in feldspathic glass (dark gray) among pyroxene (light gray). Pyrite grains (white) in globules. Note broken globule at upper left.

Carbonates. The dominant aqueous deposits in ALH 84001 are carbonate minerals, which form ellipsoids, discs, and other space-filling shapes, Figure 1 [1,4,5,6 etc]. These deposits are chemically zoned, nearly continuously from calcitic and ankeritic cores to magnesite-siderite compositions ranging from nearly pure magnesite to ~Mg45Fe45Ca10 (Fig. 2); hydromagnesite is not reported. The carbonates may have been deposited in several episodes [6,8]. The C and O isotope compositions of the carbonates vary in concert with cation compositions [6,9-11], consistent with formation by mixing of fluids. Early reports suggested carbonates formation near 700°C or from melts, but their chemical and isotopic zoning require hydrothermal to cryogenic conditions. Similar globules are reported on Earth in hydrothermal or groundwater alteration of basalt [5].

Other Primary Aqueous Effects. Associated with, and within, the carbonate globules are pyrite euhedra, rare sphalerite, and rare mica in submicron grains [12-14]. The S isotopic composition of the pyrite, δ^{34}S and Δ^{33}S, suggest formation from low-temperature fluids that had interacted with the martian atmosphere [13,14]. Carbonate globules are spatially associated with small olivine grains [15], which may mean that the carbonates occupied void spaces produced by dissolution of other olivine grains [16,17]. Irregular textures on some orthopyroxene surfaces suggest dissolution and some precipitation of clays [18], but these effects are volumetrically minor. Veinlets of silica cut the carbonates and other minerals [19].

Subsequent Shock Effects. The carbonate globules and other aqueous deposits in ALH 84001 were strongly affected by a subsequent shock event [3]. Pre-

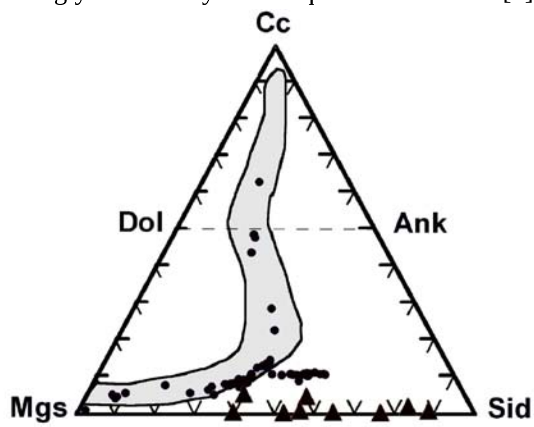

Figure 2. Carbonate compositions in ALH 84001 [7], shaded field is EMP analyses, comparable to other datasets. Dots are direct TEM analyses; triangles are spread-beam TEM of magnetite-rich areas (compositions of decomposed carbonate?).

shock void spaces (in which the globules grew [16]) were crushed, and globules were broken and transported in molten plagioclase [3]. In the thermal aftermath of the shock event [7], Fe-bearing carbonate was partially decomposed to Fe-poorer carbonate and magnetite, in shapes similar to those formed by some Earth bacteria [7,18,20-22]. Decomposition of siderite produces C-O (±H) gas species, which then reacts to form macromolecular carbon, catalyzed by the magnetite [4,7,23].

Nakhlites: All of the nakhlite Martian meteorites (augite-olivine cumulate igneous rocks) contain deposits and alterations from Martian waters [24-26], mostly as veinlets and patches of red-brown ‘iddingsite’. ‘Iddingsite’ is a sub-mm mixture of smectite clay, iron oxy-hydroxides, and salt minerals, formed by low-temperature aqueous alteration of olivine and glass (Fig. 3). Iddingsite forms veins through olivine, stringers along cracks, and masses where mesostasis or intercumulus olivine once lay (Fig. 3). Iddingsite veins in olivine typically have serrated or saw-tooth borders formed of segments along the olivines' {021} planes. The coarsest smectite is in Lafayette, where grains (to ~100 mm) radiate from vein walls. The smectite has strong basal {001} cleavage with a broad diffraction of ~1.4nm [35], indicating significant disorder in stacking and intercalation. Near the centers of the veins are thin veinlets, a few mm wide, of submicron or amorphous material of smectite composition (refs in [26], [27]). These smaller veinlets cut across the structure and cleavages of the coarser smectite grains. This same pattern occurs terrestrial 'iddingsite' (e.g., Figs. 130, 131 of [28]). The iddingsite in Lafayette and Y000593 also contains iron oxide-hydroxide material, red isotropic masses in thin section. This material is Lafayette is nearly amorphous, and some diffracts as 'two-ring ferrihydrite' (Treiman, unpublished data). The iron oxide in NWA 817 is reported to be goethite [29].

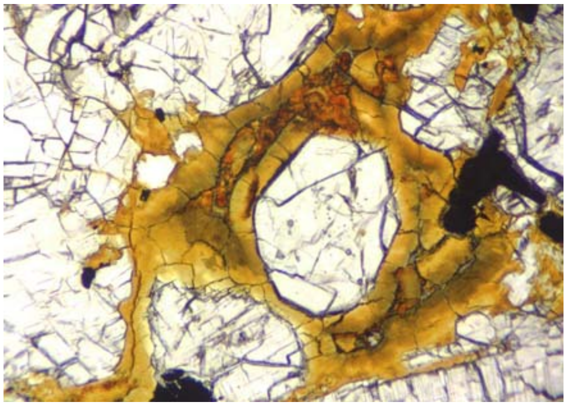

Figure 3. Iddingsite in Lafayette (plane polarized); smectite (yellow) and Fe-oxide material (red), & augite (clear) in Lafayette [26]; ~1 mm across. Iddingsite fills space among augites; smectite grains radiate inward; cores filled with round globules of Fe-oxide.

This iddingsite has a range of compositions, as can be seen on BSE imagery as bands and speckles of varying brightness. In bulk composition, iddingsite is equivalent (more or less) to mixtures of olivine, iron oxy-hydroxide, mesostasis glass, and water. Iddingsite in olivine has nearly no Al_2O_3, while that in mesostasis areas contains up to 5% Al_2O_3. Lafayette iddingsite has a REE pattern similar to that of the mesostasis, but at lower abundances [30]. Water in the iddingsite has a high $\delta^{18}O$ and a higher $\Delta^{17}O$ than the surrounding silicates – this is taken to indicate that the forming water had been in communication with Mars' surface and atmosphere [31].

Salt minerals are present associated with the 'iddingsite.' In Lafayette, there are grains or masses (to ~100 mm) of gypsum and calcic siderite [32,27]). The salt assemblage in Nakhla is more complex, with Mn-siderite, anhydrite, and halite [32]. These salts occur as unzoned, anhedral grains among feldspar and 'granitic' glass in the mesostasis, possibly associated with phosphates. MIL03346 contains gypsum associated with clay-like or amorphous material [33]. Jarosite is reported in several nakhlites, although it is not clearly pre-terrestrial. Sulfur in the sulfates [34] shows anomalous $\Delta^{33}S$, indicative of atmospheric effects.

In Nakhla, Lafayette, and Y000593, pyrite or marcasite occur with the iddingsite. Pyrite in Nakhla and Lafayette have sulfur isotope ratios near the solar-system initial, ($\delta^{34}S$ = ~3.4–+1.5‰) but with some mass-independent fractionation effects [14,34].

The biggest challenge of modeling alteration in the nakhlites will be dealing with its clay minerals, Fe-O-H phases and amorphous materials. Free energies of such materials are poorly defined, and they are subject to significant absorption and adsorption of cations, anions, and organic matter.

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