

FORMATION OF CARBONATE AND OXYHYDROXIDE MINERALS BY IMPACT OF A VOLATILE-RICH BODY. R.A. Zeigler, B.L. Jolliff, A. Wang, R.L. Korotev, D.T. Kremser and L.A. Haskin, Department of Earth and Planetary Science, Washington University, 1 Brookings Drive, Campus Box 1169, St. Louis, MO 63130. (zeigler@levee.wustl.edu)

Introduction: Sample 65903,16-7 is a 2–4 mm (16.7 mg) rocklet from an Apollo 16 rake sample. It is a slightly vesicular impact-melt breccia [1], with clasts of anorthite, grains of forsteritic olivine, and metal-phosphide intergrowths in a very-fine-grained matrix of magnesian augite, sodic plagioclase, and ternary feldspar-like glass. Geochemically, 65903,16-7 is unusual because it is very magnesian, alkali-rich, and shows evidence for both reduction to an fO_2 level of $\sim 10^{-13}$ during impact-melt crystallization and later oxidation during which carbonate and possibly FeOOH were deposited [2]. This abstract focuses on the carbonate and FeOOH. Raman spectroscopy and electron microprobe analysis (EMPA) have shown the carbonate to be siderite and the FeOOH to be goethite (α -FeOOH). On the basis of textural evidence, the carbonate and possibly the goethite formed on the Moon from a fluid derived from the vaporization of a volatile-rich impactor.

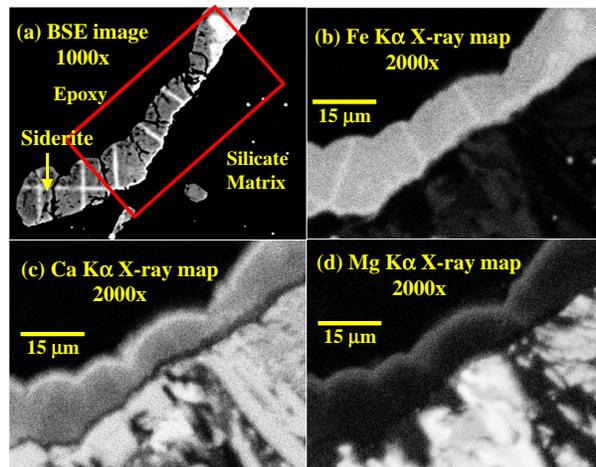


Figure 1: (a) Back-scattered electron image of an exterior siderite grain. Bright areas in the grain are EMPA damage. Field of view is $\sim 90 \mu\text{m}$. Red box is enlarged and rotated in (b), (c), and (d).

Methods: Mineral identifications and compositions were determined by reflected light microscopy, a JEOL 733 electron microprobe, and a Kaiser HoloLab5000-532 Raman spectrometer on a polished thick section made from $\sim 1/3$ of the irradiated (INAA) particle.

Petrography and Geochemistry: Most of the siderite occurs on the exterior surface of the particle as flattened, lobate grains (Fig. 1a), similar to the morphology observed in martian meteorite ALH84001 (although very different compositionally [3]) and in carbonate experiments [4]. Siderite also occurs in the interior of the particle filling fractures and vesicles (Fig. 2). Goethite occurs as submicron rims of uniform thickness between the siderite and matrix silicates (Figs. 1a,2). Some of the

smallest veins appear to consist entirely of goethite. Despite a thorough search, no FeOOH phase was observed associated with the metal-schreibersite grains.

The average composition of the siderite is $(\text{Fe}_{0.81}\text{Mg}_{0.05}\text{Mn}_{0.00}\text{Ca}_{0.14})\text{CO}_3$; it shows some compositional variation, however (Fig. 3). In general, the grains show micron-scale zoning with Fe-rich cores, becoming progressively more calcic and magnesian toward the rims (Fig. 4, Figs. 1b-d). The siderite also contains minor amounts of NiO (0.35 wt %) and S (0.15 wt % as SO_3). Because of its small size, direct analysis of the goethite without overlapping adjacent phases is not possible; an estimate of its composition was made by deconvolving analyses that overlapped goethite, siderite, and plagioclase. This deconvolution shows that the goethite has an average of 3 wt % NiO, minor S (0.6 wt % as SO_3), and trace amounts of Cl (0.2 wt %), ZnO (0.1 wt %), and PbO (0.2 wt %).

Raman Analysis: Because we do not directly measure C or OH with EMPA, we used Raman spectroscopy to verify the mineralogy suggested by EMPA. The Raman spectra obtained for the suspected carbonate in sample 65903,16-7 match the spectrum of siderite (Fig. 5a). Raman spectra of the bright rims on the siderite grains match the Raman spectrum of goethite, but not lepidocrocite (γ -FeOOH) or akaganeite (β -FeOOH; Fig.

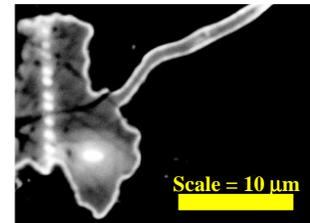


Figure 2: BSE image (3600x) of an interior siderite grain. Note the bright rim of goethite on both the grain and vein. Bright areas within the grain and vein are beam damage caused by the electron microprobe.

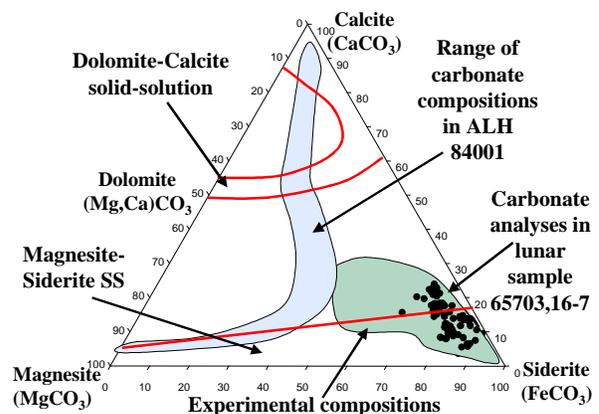


Figure 3: Carbonate ternary diagram. Carbonate compositions for ALH84001 are from [5]. Regions of solid-solution (SS) at 700°C are shown in red [6]. Experimental compositions are from [4].

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5b). The spectra of both the siderite and goethite show a range in relative peak height and width. These variations are sensitive to the degree of crystallinity of the mineral, and the variation may be due to rapid crystallization.

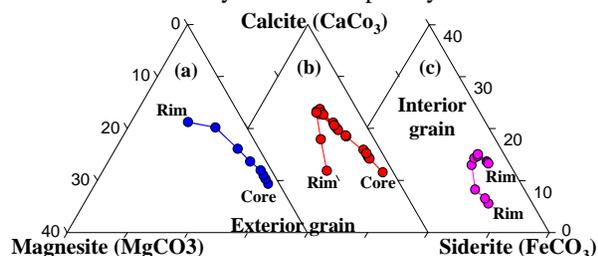


Figure 4: EMPA traverses (~1 μm step) across two siderite grains. (a) Typical zoning in exterior siderite grains. (b) Unexplained Fe rich analyses on the rim of the same exterior grain (nothing apparent in back-scattered imagery). (c) The interior grains crystallized from the edges inward and have Fe-rich rims and Ca/Mg cores.

Discussion: Carbonate or hydrated minerals formed on the Moon have not previously been confirmed; therefore, the important question is this: Did the siderite and goethite in sample 65903,16-7 form on the Moon? The answer for siderite is yes. The siderite is not an alteration product, and none of the conditions that the particle has undergone since it was collected would enable siderite to form. Whether or not the goethite formed on the Moon is less clear. Although a common alteration product of siderite is goethite [7] and this particle has been subjected to conditions that in principle could allow the formation of goethite (hot water rinse during sectioning), the overall evidence suggests the goethite did not form in this manner. Goethite is not observed on any exterior surface (in the polished section), but is found throughout the particle in <1–5 μm veinlets. The thickness of the goethite rims does not vary when in contact with different silicates, as would be expected if the matrix had been partially altered to goethite. Finally, no Fe-alteration products were observed on any of the Fe,Ni metal grains. It is unlikely that any process operating during sample transfer or sample preparation would have altered siderite to goethite without also altering the Fe,Ni metal.

Fe-oxyhydroxide has been found in Apollo 16 samples (the so called “rusty rocks” [8,9]). This FeOOH was identified as akaganeite and presumably was formed by terrestrial weathering of lawrencite (FeCl₂) and Fe,Ni metal [8]. The goethite in this sample differs from these akaganeite occurrences. The goethite is associated with siderite, not Fe,Ni metal. The average Cl levels in the goethite are an order of magnitude less than average Cl values in the akaganeite [8,9]. The goethite occurs as smooth rims on siderite in 65903,16-7, whereas the akaganeite forms blebs that appear to corrode metal.

The most likely source of the fluid that deposited the siderite is the vaporization of a volatile-rich impactor

(e.g., a comet or carbonaceous chondrite). Although the temperature and pressure of formation for siderite cannot yet be constrained, it is clear that the siderite (and goethite if it formed on the Moon) formed quickly and the source of the fluid was transient. Micron scale zoning (Fig. 4) within the siderite grains suggests the grains did not have time to equilibrate, the Raman spectral features suggest poor crystallinity caused by rapid deposition, and there is a lack of evidence of alteration of the silicate or metallic phases. Experimentally produced siderite of comparable size, composition, and morphology (Fig. 3) precipitated at 125°C in 24 hours [4].

References: [1] Korotev R.L. (1994) *GCA*, 58, 3931-3969. [2] Zeigler R.A. et al. (2001) *LPS XXXII*. [3] Mittlefehldt D.W. (1994) *MAPS* 29, 214-221. [4] Golden D.C. et al. (2000) *MAPS* 35, 457-465. [5] Harvey R.P. and McSween H.Y. (1996) *Nature* 382, 49-51. [6] Anovitz L.M. and Essene E.J. (1987) *J. Petrol.* 28, 389-414. [7] Deer W.A. et al. (1999) *Rock-Forming Minerals*, 579. [8] Taylor L.A. et al. (1974) *Geology* 1, 429-432. [9] El Goresy A. et al. (1973) *EPSL* 18, 411-419. **Acknowledgements:** This work was sponsored by NASA grant NAG5-4172 (LAH). We would like to thank Gretchen Benedix for her insightful comments and suggestions.

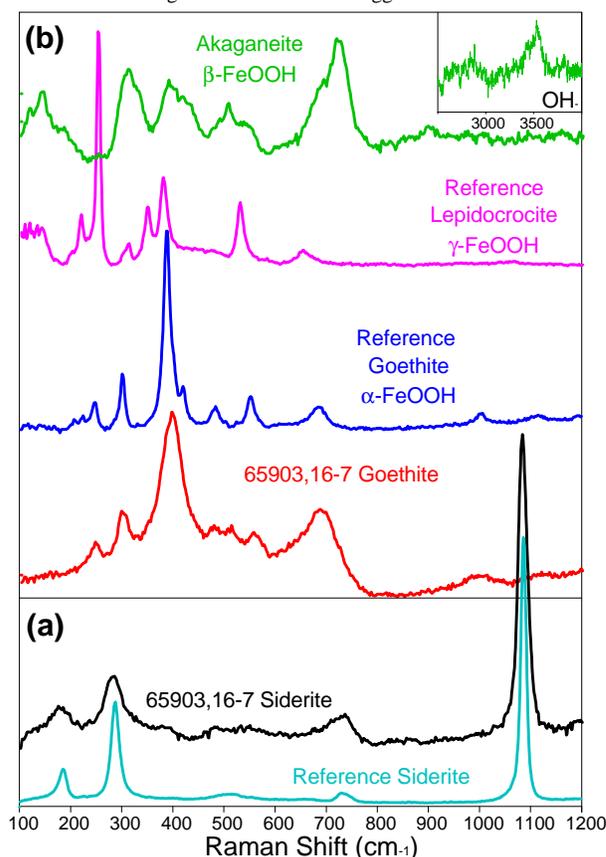


Figure 5: (a) Raman spectra of the siderite of this sample (background subtracted) and a reference siderite. (b) Goethite of this sample compared to reference goethite and lepidocrocite and spectra of suspected akaganeite, FeO(OH,Cl) alteration on metal in sample 66055,155 (background subtracted). Inset (top right) is a suspected OH- peak in the akaganeite.