CARBONATES IN THE MARTIAN METEORITE, ALH84001: WATER-BORNE BUT NOT LIKE THE SNCs. Susan J. Wentworth¹ and James L. Gooding². ¹C23, Lockheed Engineering and Sciences Co.; ²SN2, NASA Johnson Space Center, Houston, TX 77058 USA.

The origin of carbonates in ALH84001 is significantly constrained by Fe-sulfate and ZnS accessories. Unlike previously documented occurrences of Ca-Mg-carbonates in shergottites, nakhlites, and Chassigny (SNCs), which indicate paragenesis from cold to warm, highly oxidizing water, the Ca-Mg-Fe-carbonates in ALH84001 apparently formed from water under chemically reducing, and possibly hotter, conditions. Reducing conditions and elevated temperatures might account for the surprising lack of secondary silicates and oxides in ALH84001.

**Introduction.** Allan Hills, Antarctica, 84001, which is the most recently recognized member of the Martian meteorite clan, is distinguished by submillimeter-sized grains of indigenous Ca-Mg-Fe-carbonate minerals [1]. Although micrometer-sized carbonates have been identified previously in the shergottite-nakhlite-chassignite (SNC) meteorites (see review in [2]), the larger and more abundant carbonates in ALH84001 are accessible to a wide variety of analytical techniques. Stable-isotope analyses and interpretations have proceeded with vigor [3], but the paragenetic context of the carbonates in ALH84001 has remained unclear. Our studies seek the broader secondary mineralization history of ALH84001, including the physical and chemical conditions of carbonate formation, through identification and geochemical modeling of all secondary minerals.

**Samples and Methods.** Our investigation followed the strategy previously developed for secondary minerals in SNCs (see review in [2]). Both interior and exterior (fusion-crusted) pristine chips, as well as a polished thin section, were studied by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS), including direct analysis of carbon and oxygen using a thin-window detector.

**Results.** The fusion crust of ALH84001 is remarkably free of salts and clay-mineraloids that are common terrestrial weathering products in Antarctic meteorites as described elsewhere [4]. In fact, we documented only a single occurrence of Ca-sulfate (probably gypsum, CaSO₄·2H₂O) as a clear indicator of terrestrial chemical weathering. Therefore, secondary mineralization in ALH84001 can be studied with relatively little interference from terrestrial weathering.

Possible Fe-sulfates occur in association with Fe-sulfides and Cr-spinels that contact carbonates (Fig. 1). The Fe-sulfates are recognized by textural contrasts and changes in the Fe/S/O interelemental ratios, relative to their primary-mineral hosts. The sulfates are not the same as, and do not appear related to, the Fe-rich rims on carbonates as found by [1]; the latter rims contain only a little S. We also found ZnS as an inclusion in carbonate (Fig. 2). For both the Fe-sulfate and ZnS, mineral textures indicate paragenesis involving oxidation-reduction reactions in aqueous solutions. The nearly spherical, but feather-edged, morphology of the ZnS (Fig. 2) suggests one of two principal modes of origin: (1) the ZnS crystallized as a primary igneous sulfide, then survived post-magmatic precipitation of carbonates that locally replaced the original silicate host; (2) the ZnS is an insoluble co-precipitate from the same mineralization event that formed the carbonate. Hypothesis (1) predicts that ZnS globules should be found in primary silicates that escaped carbonate mineralization; however, we have found no such occurrences to date. Hypothesis (2) suggests that the ZnS/Ca,Mg,Fe-carbonate association represents an assemblage that defines at least one P-T-X condition during carbonate formation; this hypothesis is favored by the complete enclosure of ZnS in carbonate (Fig. 2).

In the HCl-H₂O-CO₂-H₂S-ZnO system, the ZnS/ZnCO₃ reaction boundary varies as a function of \( f(CO₂) \) as well as \( a(HS⁻) \) and \( a(H⁺) \) [5]. For constant pressure, the ZnS stability field shrinks with increasing temperature; for constant temperature, it expands with decreasing pressure [5]. If the activity of CO₂ in water equilibrated with the Mars atmosphere is on the order of \( a(CO₂) = 10^{-2.3} \) [6], then replacement of ZnS by ZnCO₃ (perhaps as Zn dissolved in Ca,Fe-carbonate) would be thermodynamically favored for all solutions with ion products of \( a(HS⁻)a(H⁺) < 10^{-22} \) at 25-300°C [5]. In Eh-pH space, coexistence of ZnS with Ca,Mg,Fe-carbonates implies pH > 7.8 and Eh < -0.1 [7]. In fact, stabilization of Fe-rich carbonates implies an oxidation potential near Eh = -0.2. Therefore, it is unlikely that primary ZnS
would have survived invasion by a carbonate-forming fluid if the system had reached equilibrium under oxidizing conditions. Coexistence of Fe-sulfate with Fe-sulfide and Ca,Mg,Fe-carbonate indicates pH > 7 and -0.2 < Eh < 0 [7]. The basic pH should have favored silicate clay formation but clay formation might have been inhibited by either the reducing chemistry or unfavorably high temperatures.

**Conclusions.** Aqueous alteration of ALH84001 differed from that affecting the SNCs. Absence of secondary silicates, Ca-sulfate, and major Fe-oxide “rust” from ALH84001 demonstrates strong deviation from nakhlite- and shergottite-type alteration; occurrence of Fe-bearing carbonates and sulfates in ALH84001 shows substantial deviation from Chassigny-type alteration. The well-developed carbonates in ALH84001 are distinguished by ZnS and Fe-sulfate accessories that constrain solution chemistry to reducing conditions at temperatures that were probably less than 300°C but still warmer than those of SNC-type solutions.

**References.**


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**Figure 1.** Secondary electron images of Fe-sulfates (arrows) in polished thin section ALH84001,86 (left) and pristine interior chip ALH84001,117 (right). Scale bars are in micrometers.

**Figure 2.** Back-scattered electron images of ZnS (arrows) in pristine interior chip ALH84001,117. Scale bars are in micrometers. The ZnS occurs at the interface of Mg-rich and Mg,Fe-rich carbonates within pyroxene (px). The meandering vein (v) contains enhanced S and Cl concentrations.