Carbonates in ALH 84001: Part of the Story of Water on Mars

--- The study of multi-generational carbonate assemblages in Martian meteorite ALH 84001 reveals a complex history of crystal formation, growth, and alteration.

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Carbonate-rich regions in ALH 84001 are complicated. There are familiar forms of carbonate as well as fascinating textural forms previously unreported including carbonate rosettes, planiform "slab" carbonates, distinct "post-slab" magnesium carbonates (magnesite), and carbonates interstitial to feldspathic glass and orthopyroxene. Slab carbonates reveal portions of the carbonate growth sequence not seen in the rosettes and suggest that initial nucleating compositions were rich in calcium. They formed in two major stages. The first stage involved growth of the rosettes and slab carbonates. This step was controlled by the rate of crystal nucleation, how fast the ingredients were delivered to the growing crystals, and how much fluid was available. Cosmochemists call this type of growth "kinetically controlled." Next, an alteration event formed the magnesite-siderite (iron carbonate) layers on the exterior surfaces of the carbonate. Post-slab magnesite, intimately associated with silica glass, is compositionally similar to the magnesite in these secondary exterior layers, but represents a later generation of carbonate growth. Formation of feldspathic glasses had little or no thermal effect on carbonates, as indicated by the lack of thermal decomposition or any compositional changes associated with glass/carbonate contacts.

The carbonates tell an important story about water in the ancient crust of Mars. The presence of numerous, distinct generations of carbonate formation and relatively clear fracture chronology within carbonate further suggest that interactions between ALH 84001 and the crustal fluids of Mars were discontinuous and occurred only a few times over its 4.5 Ga history. The reactivation and remobilization of fluids (causing events such as formation of magnesite-siderite-magnesite layers and precipitation of post-slab magnesite) and the fracturing within the rock were almost certainly driven by impacts. The evidence for punctuated, impact-driven interaction between rocks and fluids supports scenarios describing temporary hydrous environments as opposed to those including large-scale, long-term hydrologic systems including oceans. Therefore, unless ALH 84001 is a particularly rare sample that escaped intense alteration, the hydrosphere of Mars may not have interacted with the rocks as thoroughly as planetary geologists have inferred from the presence of river networks and other features formed by flowing water.
Water on Mars

A central goal of the Mars Exploration Program is to understand the history of water on Mars. We need to know how much there is now and was soon after the planet formed, how it cycles through the crust, where it resides now, how much is in magmas produced in the mantle and how it varies throughout the mantle, and how it has shaped the surface of the planet. The quest to understand all about water on Mars is part of a larger effort to determine if the planet was ever habitable enough for life to have originated and evolved. (Detailed goals for the exploration of Mars have been developed by the Mars Exploration Program Analysis Group, MEPAG, and can be found at the MEPAG web site. Link opens in a new window.)

Planetary geologists have identified numerous features that indicate that vast amounts of water sculpted the Martian surface: valley networks, huge outflow channels, layered sediments, and recent gullies. There might even have been an ocean in the northern lowlands of Mars. Recent observations by the Opportunity rover in Meridiani Planum show that water reworked sediments and deposited a sequence of minerals as it evaporated. Cosmochemists have calculated that the salty water that made all these impressive features would have evaporated to produce vast quantities of carbonate minerals. However, observations by the Thermal Emission Spectrometer onboard the Mars Global Surveyor spacecraft indicate that there is only a few percent of carbonate on the surface. Martian meteorites contain a little carbonate, which studies show formed on Mars, not after their arrival on Earth, but the amount is very small. Clearly we are missing something important. Martian meteorite ALH 84001 has the most carbonate of any Martian meteorite, so it might hold the key to understanding carbonate formation on Mars. The carbonates in ALH 84001 are an important part of the story of water on Mars.
An Important but Confusing Meteorite

Following its identification in 1994 as a Martian meteorite by David Mittlefehldt (Johnson Space Center, JSC), Allan Hills (ALH) 84001 was rapidly recognized as being a very important sample of the Martian crust (pictured on the right). Its fame exploded with the publication of a paper in 1996 by David McKay and his colleagues from JSC, Stanford University, and McGill University that said the meteorite contained evidence for life on Mars. [See PSRD article Life on Mars?] This announcement led to a huge number of studies designed to test this interpretation. [See the PSRD archive of articles on Mars Life Issues.] Whether it contains fossil life or not, ALH 84001 was affected by water-bearing fluids while it was still home in the ancient crust of Mars. ALH 84001 is by far the oldest of the Martian meteorites (~4.5 Ga). ALH 84001 is a cumulate orthopyroxenite, which means it is loaded with a mineral called orthopyroxene. The orthopyroxene is accompanied by some chromite, feldspathic glass, augite, apatite and olivine. It formed when a magma invaded the juvenile Martian crust. As the magma crystallized, orthopyroxene accumulated in the magma. Slow cooling in a big magma body allowed time to make big crystals, so it is coarse grained. However, it has a cataclastic texture, indicating that it has been exposed to a series of impact shock events that partly demolished the original igneous texture. This intense shock metamorphism has resulted in the presence of crushed zones, or granular bands, that contain crushed orthopyroxene, chromite, feldspathic glass, olivine and other phases, including the all-important carbonates that Ralph Harvey (Case Western Reserve University) and I studied.

Despite being one of the most studied rocks of all time, we do not understand its complex
history. Many distinct geologic stories have been told for ALH 84001. Most agree on initial crystallization as part of a slow-cooling underground magma chamber, and that the rock gained its current, highly fractured state during several post-crystallization impact events. The time between impacts is not known. The resultant fractures provided conduits for the passage of fluids through the rock, and allowed the development of secondary, non-igneous minerals within them.

The secondary minerals are of particular interest in ALH 84001 because they offer physical and chemical clues to past Martian environments. Carbonate minerals are the dominant secondary phase in ALH 84001, making up ~1% of the rock. They occur in a variety of settings and textures, from interstitial crack fillings to conspicuously zoned clusters, semi-circular in cross-section, which have gotten the name "rosettes." ALH 84001 rosettes vary in composition concentrically from Ca-rich near the center through dolomite-ankerite (Mg-rich) to alternating magnesite-siderite-magnesite (MSM) layers at the outer edges, the siderite layers of which often contain fine, single-domain magnetite, a central part of the debate about evidence for life in the meteorite.

The ages of the carbonates are difficult to determine, but careful work by Grenville Turner (University of Manchester) and colleagues and Lars Borg (University of New Mexico) and colleagues indicate an age of 3.83 Ga to ~4.04 Ga, coincident with the period of heavy bombardment in the inner solar system prior to ~3.8 Ga. On the basis of their textural setting in the rock and on their ages, it is safe to conclude that carbonate formation clearly post-dates both initial igneous crystallization and an initial episode of fracturing by impact.

Cosmochemists are still debating how the carbonates formed. Proposed formation scenarios include low-temperature aqueous precipitation, evaporative processes, high-temperature reactions, and impact-induced melting. Recent experimental studies by D. C. Golden (Hernandez Engineering Inc., Houston) and colleagues at JSC confirm that low-temperature precipitation (150 °C) from a saturated fluid followed by short-term heating can reproduce many of the carbonate features seen in ALH 84001.

Uncertainty also lies in whether there were single or multiple generations of carbonate formation and the role, if any, of alteration after it had formed. Adrian Brearley (University of New Mexico) suggested that some nanometer-scale mineralogy and textures in ALH 84001 result from thermal decomposition of pre-existing carbonate materials, particularly siderite decomposition to magnetite. The experiments of D. C. Golden and colleagues showed that subsequent heating of carbonates formed in the laboratory (to 470 °C) was adequate to form magnetite crystals. Alternatively, Kathie Thomas-Keprta (Lockheed Martin) and her colleagues at JSC still believe that at least a subset of the tiny crystals of magnetite in ALH 84001 were made by Martian microorganisms.

The carbonate minerals in ALH 84001 record part of the story about water in the ancient Martian crust, but the complexity of the carbonates and the drastically different interpretations of how they formed obscure the story. Ralph Harvey and I tried to clear up the confusion by studying several complex, carbonate-rich regions in ALH 84001. We examined forms of
carbonate familiar to cosmochemists who had studied ALH 84001, as well as more complete exposures of carbonate growth sequences. We placed our observations into context with previous work, offering insight into the complicated story of carbonate formation in this unique and important meteorite.

What the Carbonates Look Like

The regions examined in this study revealed a variety of textural relationships ranging from simple to complex, with carbonate, feldspathic, and silica glasses being the most significant phases. Carbonate occurs as the commonly described, photogenic rosettes, and in three other forms seen previously but not described or classified in a uniform way. These are discrete, layered packages here termed "slab" carbonates, massive background fill ("post-slab magnesites") and carbonate occurring "interstitial" to feldspathic glasses and orthopyroxene.

**Rosettes.** Rosettes were found only in ALH 84001,303 (see image above). These rosettes are identical to those described and analyzed in many previous studies of ALH 84001, with semi-circular cross-sections and distinct, consistent and concentric chemical zoning. This
zoning includes alternating magnesite-siderite-magnesite (MSM) layers on the outer portions of the carbonate sequence.

**Slab.** We identified a previously undescribed form of carbonate, which we termed "slab" carbonate. It figures prominently in both of the regions studied in detail. These slab carbonates are elongate packages that conform to fracture faces and exhibit chemical zoning distinctly visible in backscattered electron images taken with an electron microprobe, duplicating zoning commonly seen in rosettes. (See images above.) This zoning, however, is parallel to the faces of the slab (instead of concentric around a central point) and exhibits a more complete chemical zoning record with sharper contacts between compositional zones. Slab carbonates include a thin, Ca-rich layer (bright in the electron images) at one edge and the familiar magnesite-siderite-magnesite (MSM) layers at the opposite edge, with three consistently distinct layers found between. Slab carbonates are typically highly fractured, in a manner indistinguishable from that seen in rosettes, with fractures generally crossing all layers. (See image below.) Like rosettes, slabs show no obvious preferential association with specific mineral species. They are found in contact with orthopyroxene, feldspathic glass, and other carbonates.
**Post-slab magnesite.** The regions studied here contain almost pure magnesite that is texturally distinct from carbonate in rosettes or slabs. We refer to these carbonates as "post-slab magnesites" as we believe they formed as a distinct generation, post-dating zoned slabs, rosettes, and magnesite-siderite-magnesite (MSM) layers. Post-slab magnesites occur as numerous blebs or grains, semi-circular in cross section (see "PSM" in the images above). They do not appear to be the outer edges of rosettes, and are smaller and more uniform in size. These carbonates entrain small fragments of other minerals, including other carbonates. Post-slab magnesites have a fracturing habit different from the zoned carbonates, with fractures formed around individual blebs, and rarely crossing through them.

In the regions we studied, we found post-slab magnesite in contact with the high-Ca end of the slab carbonate (bright in the photographs). It occurs with silica glass and mixed with fragments of other phases. Silica glass tends to be associated with fractures surrounding post-slab magnesite blebs, and occasionally occurs as larger irregular blebs (see image below).
Backscattered electron image of post-slab magnesite (PSM) in ALH 84001,302 showing blebby texture of carbonate, silica glass (Si) rims around black carbonate blebs, and larger blebs of silica glass. This image was contrast enhanced to better show the mottled texture within the post-slab magnesite region. Slab carbonate (Slab), orthopyroxene (Opx), and feldspathic glass (Fs) are also labeled.

**Interstitial carbonate.** We treated carbonate interstitial to larger domains of other minerals, particularly feldspathic glass and comminuted orthopyroxene, as a separate category called interstitial carbonate (see "IC" in the images above). Some carbonates appear to have been mechanically entrained by feldspathic glass, which accounts for a significant portion of the mineral inventory in the regions we studied. Carbonates found in the interstices of orthopyroxene surrounding the secondary mineral regions are similar in appearance to those found entrained within feldspathic glasses. The carbonates in orthopyroxene have been described previously.

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**What the Carbonates are Made Of**

I measured the composition of the carbonates using an electron microprobe. The diagram below shows ~800 carbonate analyses from these sections. The data are plotted on a triangular diagram, called a ternary diagram. Each corner of the triangle represents the pure composition of a mineral. All data are plotted as molar abundances of MgCO₃, CaCO₃ and FeCO₃. The distance from a corner gives the abundance of that chemical component in a mixed mineral.
Ternary diagram of major element compositions of all carbonates I measured in ALH 84001, 302 and ALH 84001, 303 and individual textural groups.

My new analyses overlap and extend compositional ranges previously reported for ALH 84001 carbonates. These new data show a much more continuous compositional trend filling gaps seen in previous work, including significant proportions of high-Ca carbonate that were seen only sporadically in previous studies.

Ternary diagrams of major element compositions of carbonate rosettes (left) and slabs (right). Compositions from the interiors of rosettes (more central to the ternary) are clearly distinguishable from those in the magnesite-siderite-magnesite (MSM) rims (seen at the MgCO₃ apex). Compositions of slab carbonates span the entire range of compositions.
Compositions of slab carbonates differ from rosettes only in that they exhibit a wider range of values, varying in a nearly continuous sequence across the ternary compositional diagram (see diagrams above). The sharp boundaries between layers seen in backscattered electron images also correspond to measured compositional changes. Point analysis transects were constructed approximately perpendicular to zoning across slab carbonates in one of the samples studied and ALH 84001,302 revealing a consistent sequence of compositional variation. This sequence suggests that the compositional sequence seen in carbonate rosettes is a subset of that seen in slab carbonates.

The massive, space-filling post-slab magnesites span a wider compositional range than magnesites in the magnesite-siderite-magnesite layers of rosettes, from nearly pure MgCO₃ to intermediate compositions. The interstitial carbonates are not chemically distinct. Their compositions span nearly the entire range, though most are intermediate, suggesting that they represent a combination of all observed carbonate sources (see diagrams above).

**How the Carbonates Formed**

The concentric zoning of the rosettes suggests that they formed in small pockets of water by nucleating (forming a seed crystal) in one place and growing from it to fill up the space until the water was used up. As the rosettes grew, their formation changed the composition of the surrounding water, causing them to become chemically zoned. They nucleated on any other crystal (large orthopyroxenes, crushed orthopyroxene, feldspar) and do not appear to have reacted with the other minerals. This type of crystal growth producing zoned crystals is called
kinetically controlled—the growth is governed by the abundance and speed of delivery of the raw materials to the growing carbonate crystals.

The textures of microcrystalline slab carbonates are also consistent with formation under kinetically controlled conditions. Slab carbonates show visible zoning parallel to fracture surfaces, suggesting nucleation from numerous, closely spaced points on a surface instead of from widely spaced individual points. The identical zoning in rosettes and slabs suggests that they formed during the same growth event; the difference between the two forms relates to the amount of available space. Essentially, when there is sufficient fluid volume (i.e., in larger fractures) slabs will form, while rosettes will form when volume is limited.

Slab carbonates are of particular value in understanding the sequence of carbonate crystallization. Their semi-planar geometry offers an advantage in that a random slice through a slab is more likely to intersect the full range of compositions present in three dimensions than is a slice through a rosette. Slab carbonates should thus provide a more complete history of carbonate formation, exposing compositions representative of early stages of formation (high-Ca layers) rarely seen in rosettes.

A Five-Step Sequence of Events

Our observations lead us to propose the history of carbonate formation shown in the diagram below. Initial formation of the rock as a cumulate orthopyroxenite was followed by impact events resulting in an initial set of fractures within the rock. A carbonate growth stage occurred next, during which rosettes and slab carbonates were precipitated into the fractures from water super-saturated in carbonate components. We do not know where the water came from, but it seems clear that the rock and its surroundings were not saturated in water for a long time because of the low abundance of carbonates and very limited alteration of the original igneous minerals. Rosettes arose from isolated nucleation sites in relatively small fractures, forming pancakes where perpendicular growth was limited and more spheroidal shapes where space allowed. Slabs nucleated in rare, larger fractures. Earliest formed carbonates were Ca-rich, but crystallization progressed toward more Mg- and Fe-rich compositions. Occasional recharge of fluids during carbonate growth altered the cation concentrations resulting in the variable compositions visible as zones in the backscattered electron images shown above.
The chemistry, mineralogy, and textures of carbonate lead us to favor a thermal event as the mechanism for forming the magnesite-siderite-magnesite (MSM) layers (as suggested by Adrian Brearley of the University of New Mexico, and others) rather than a dramatic change in the chemical composition of the fluid. We suggest that this event caused the conversion of an exterior, Mg- and Fe-rich carbonate composition into the residual MSM layers, which may have involved replacement or dissolution and redeposition of carbonate materials. The original carbonate growth trend from high to lower Ca compositions (slabs) was replaced with carbonates of relatively constant Ca and widely varying proportions of Fe and Mg (MSM). This

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<th>Event</th>
<th>Carbonate Chemistry</th>
<th>Textures</th>
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<tr>
<td>Fracturing of original rock</td>
<td>CaCO₃ (none)</td>
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<tr>
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<td>MgCO₃</td>
<td>fs</td>
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<tr>
<td>- feldspar to glass</td>
<td>FeCO₃</td>
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<tr>
<td>Initial carbonate deposition</td>
<td>A</td>
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<tr>
<td>- rosettes and slabs</td>
<td>B</td>
<td>cb</td>
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<td>- groups A-C, D?</td>
<td>C</td>
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<td>MSM deposition</td>
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<td>- group E</td>
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<tr>
<td>Further fracturing and offset</td>
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<td>Opening of fracture</td>
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<td>Post-slab magnesite &amp; Si glass deposition</td>
<td>E</td>
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<td>- group E</td>
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<td>Further fracturing</td>
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<td>Intrusion of feldspathic glass</td>
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<td>- shearing of cb from opx walls</td>
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event would have occurred with the earliest slab carbonates still attached to nucleation surfaces, as these innermost compositions appear to be unaffected by alteration. In addition, MSM layers are found concentric only around the exteriors of zoned carbonates, which would have required free space between these surfaces and the fracture walls.

Textures suggest that post-slab magnesites represent a distinct precipitation event that took place after the MSM sequences formed and before feldspathic glass intruded. Most fractures crossing slab carbonates and MSM layers do not cross into post-slab magnesites. Entrainment of slab carbonate material into post-slab magnesites also suggests that these magnesites formed after rosettes and slabs. Post-slab magnesites are physically mixed with silica glasses, suggesting that either the two phases were emplaced during the same event or silica glass precipitated after post-slab magnesite.

Unlike MSM bands, post-slab magnesites are found in contact with the oldest (earliest formed) slab surfaces. The Ca-rich edges of the slab must have been detached from their original nucleation surfaces allowing space for post-slab magnesite to precipitate. Chemically, MSM magnesites and the post-slab magnesite are similar suggesting that they formed either by similar processes or that they represent two stages of a single event. The first decomposed existing carbonates and deposited the MSM rims, while the second precipitated the chemically similar post-slab magnesites and silica glass, filling in the trend with compositions lost during the first event.

The final step involves the injection of feldspathic glass. There are numerous occurrences of zoned carbonates and post-slab magnesite entrained by feldspathic glass. In addition, there exist locations where fractures transcend the boundaries between both types of carbonate but do not cross into feldspathic glasses. These observations indicate that feldspathic glass was the last phase to enter these fractures. The bulbous texture and lobate contacts with post-slab magnesite suggest that feldspathic glass was mobile and flowed into these fractures. Feldspathic glass intrusion produced physical effects but did not seem to cause significant chemical changes. Glass intrusion further widened the fractures, entraining phases already present in fractures and further peeling some carbonates from their nucleation sites. The intrusion of feldspathic glass separated the slabs in ALH 84001,303, as well as the attached post-slab magnesites.

Other investigators have suggested that injection of the feldspathic glass caused heating and decarbonation of pre-existing carbonate. Our observations contradict this interpretation. The feldspathic glass could not have caused the heating because the sequence of events we deduced from our study indicates that the glass formed last. It was not around when the MSM layers formed. MSM sequences are present around the exterior of zoned carbonates, but neither slabs nor rosettes are consistently altered everywhere they are in contact with feldspathic glass, contrary to what would be expected if feldspathic glass was responsible for MSM formation. The variation in composition of carbonates interstitial to feldspathic glass is strong evidence that they are unaltered, mechanically entrained materials, as opposed to post-intrusion precipitates. In addition, many occurrences of slab carbonates are not visibly in contact with feldspathic glass, yet still have MSM sequences.
Why did the injection of hot feldspathic glass not cause extensive heating? Studies of glass rheology may provide a solution to this paradox—it might not have been hot. Although most researchers studying ALH 84001 assume that mobilization of feldspathic glass requires high temperatures, experiments have shown that when silica glasses are exposed to high static pressures (more than 10 times the pressure at the surface of the Earth) their viscosity (resistance to flow) can drop many orders of magnitude without significant temperature elevation. Subsequent shear then easily deforms the glass with little thermal consequence. Impact events generating 45-60 GPa of pressure provide more than enough stress needed to reach this transition. As a result, feldspathic glass can flow on the millimeter scale (as suggested by textures seen in ALH 84001) in the absence of a thermal pulse. The impact event(s) that mobilized the feldspathic glasses seen in the regions studied here likely provided enough shear strength to allow the glass to flow into the fractures at low temperatures.

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**Implications for the Ancient Martian Crust**

The presence of numerous, distinct generations of carbonate formation and relatively clear fracture chronology within carbonate show that interactions between ALH 84001 and crustal fluids on Mars were discontinuous and occurred only a few times over its 4.5 Ga history. The reactivation and remobilization of fluids (causing events such as MSM formation and precipitation of post-slab magnesite) and the fracturing within the rock were almost certainly caused by impact. The evidence for punctuated, impact-driven interaction between rocks and fluids supports scenarios describing temporary hydrous environments as opposed to those including large-scale, long-term hydrologic systems including oceans. Therefore, unless ALH 84001 is a particularly rare, particularly pristine sample, the hydrosphere of Mars may not have interacted with the rocks as thoroughly as planetary geologists infer for Mars. Geologists see clear evidence for not only river networks, but for erosion of them. Such a warm, wet period could have pervasively altered rocks in the ancient highlands, yet ALH 84001 was clearly not significantly affected by a period in which Mars was warm and wet. This could mean that ALH 84001 is just a lucky survivor. The inconsistency between photogeological and rock data needs to be reconciled before we understand the details of the history of water on Mars.

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**Additional Resources**


