

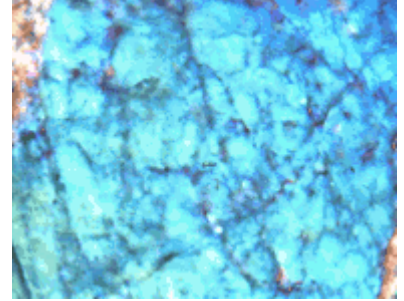
Hot Idea

posted May 13, 2002

Resolution of a Big Argument About Tiny Magnetic Minerals in Martian Meteorite

--- Magnetic minerals in Martian meteorite ALH 84001 formed as a result of impact heating and decomposition of carbonate; they were never used as compasses by Martian microorganisms.

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Shock damaged pyroxene crystal from ALH 84001 in the polarizing light microscope. Image credit: E.R.D. Scott.

Tiny grains of magnetite, an iron oxide mineral, from a Martian meteorite are markedly similar in size, shape, and composition to the little oxide magnets used by bacteria on Earth and different from other naturally formed magnetites. Is this good evidence for life on Mars? Or did the Martian magnetite grains form by another process? Our studies reveal that the planes of atoms in the Martian magnetites are aligned with atomic planes in the carbonate in which the magnetites are embedded. This shows that the magnetites formed in the rock and not inside microorganisms.

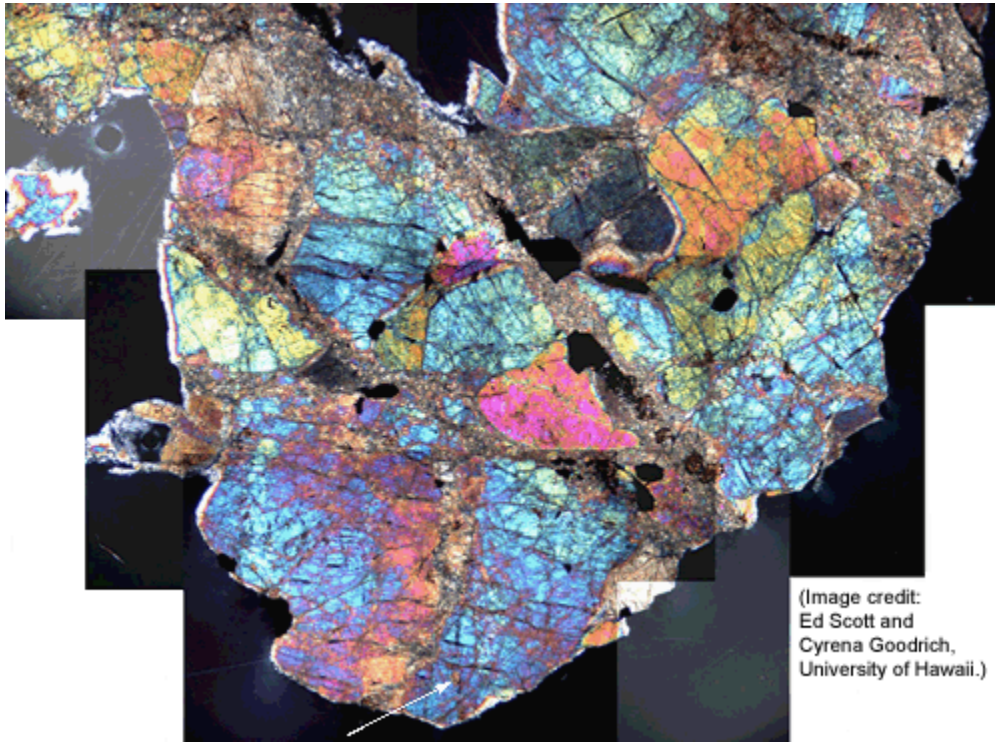
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Magnetite crystals in ALH 84001

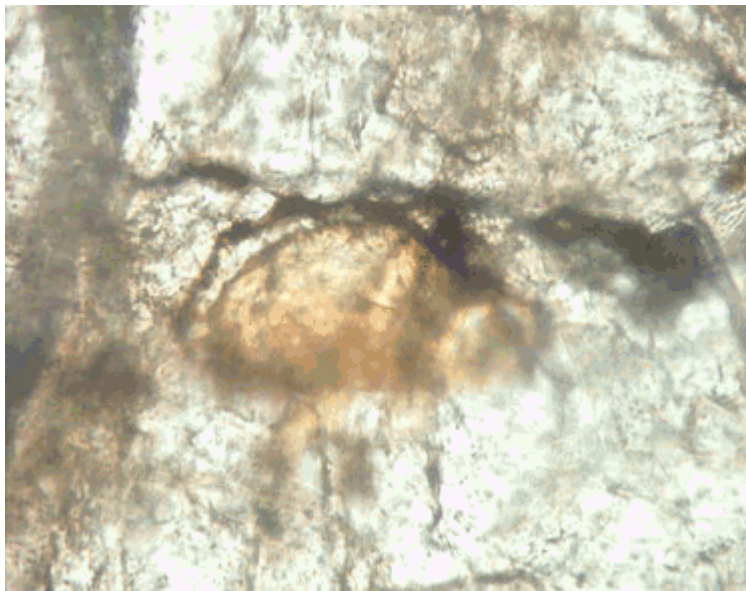
Since the startling report in 1996 of possible evidence for life in the Martian meteorite ALH 84001 [See [PSRD](#) article: [Life on Mars?](#)] attention has increasingly focused on the origin of the meteoritic magnetite, as this mineral appears to provide the most compelling evidence for biogenic activity. The magnetite grains reside in tiny grains of iron-magnesium-calcium carbonates, which are typically 50-200 micrometers across and are dispersed throughout the ALH 84001 meteorite as disk-shaped or spheroidal grains, or, in the case of carbonates that enclose silicate fragments, as irregularly shaped grains.



(Image credit:
Ed Scott and
Cyrena Goodrich,
University of Hawaii.)

Mosaic of transmitted light images of a thin section of ALH 84001 between crossed polarizing filters. The pyroxene crystals are transformed into a kaleidoscopic display of colors that help us to decipher the history of the rock. The gray criss-crossing bands are shattered pyroxene crystals that formed when an impact on Mars squeezed the rock, momentarily twisting and tearing the crystals. Black chromite crystals were also wrenched apart by the impact. The white arrow near the bottom of the mosaic marks a carbonate disk (shown below) that formed in a fracture. Maximum width shown of this mosaic is 8.5 millimeters.

The magnetites are too small to be seen using optical microscopes as they are 4-100 nanometers in size. (The smallest magnetites are about as wide as 15 oxygen atoms.)



This simple movie of a truncated carbonate disk with a pale orange core was made from thirteen separate micrographs of a thin section of ALH 84001. The carbonate is about 130 x 4 micrometers in size and is embedded inside a greyish-white pyroxene crystal. The movie shows how a change in focus of the microscope reveals that the carbonate disk formed in an inclined fracture in the pyroxene crystal. The magnetite crystals are concentrated in the two concentric black lines near the rim of the carbonate disk. (Image credit: Ed Scott.)

Kathie Thomas-Keprta (Lockheed Martin) and her colleagues at the NASA Johnson Space Center have used electron microscopes to analyze the composition and morphology of the magnetite crystals in considerable detail. Studies of thin slices of the rock show that the magnetites are found at the rims of carbonate grains in optically opaque regions and throughout the interior of the carbonate grains. By dissolving 600 magnetite crystals out of the carbonate, they found that about 25% were faceted crystals with width/length ratios of >0.4 (called elongated prisms), ~65% were irregularly shaped and 7% were more elongate with width/length ratios of <0.4 . Thomas-Keprta and her colleagues showed that the elongated prisms were remarkably similar in size, shape, and composition to the magnetites made by one strain of bacteria that uses chains of single-domain crystals of magnetite as a compass to aid in navigation. Since the bacterial compasses are made with great precision and efficiency and appear to differ from abiogenic magnetites in shape and composition (but not size), they interpreted the elongated prism magnetites as Martian fossils.

Although all workers agree that the magnetites in ALH 84001 were formed on Mars and may contain an important record of an ancient Martian magnetic field, many have argued against a biological origin for the magnetites. Peter Buseck (Arizona State University) and coworkers have questioned whether the putative Martian biogenic magnetites and the bacterial magnetites are identical in shape. John Bradley (Georgia Institute of Technology) and colleagues concluded that magnetites with width/length ratios of ~0.1 to 0.2 grew on the surface of the carbonate because their crystal lattices are aligned where they make contact. They inferred that these so-called whisker-shaped magnetites could not have been made by bacteria but had condensed from a vapor above 120°C. Thomas-Keprta and colleagues did not dispute that these magnetites were probably abiogenic. However, they argued that whisker-shaped magnetites formed at lower temperatures in the interior of the carbonate grains whereas the elongated prisms were concentrated in the opaque rims by a different process.

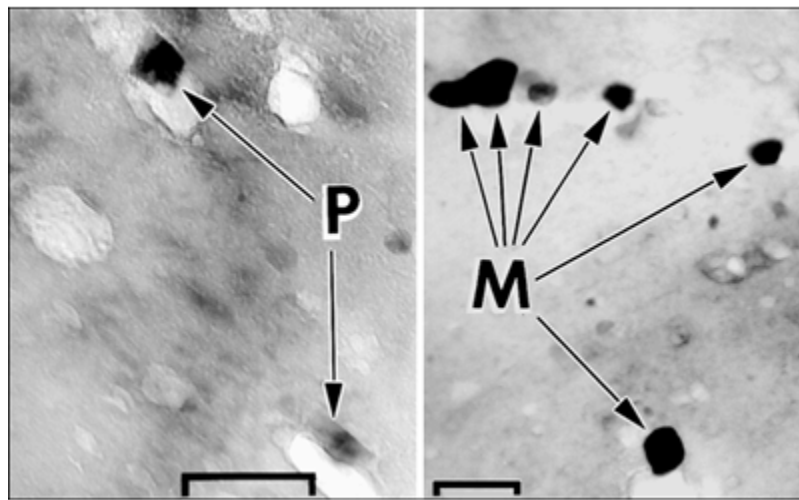
At the March 2002 Lunar and Planetary Science Conference in Houston, many speakers discussed possible origins for the magnetites in ALH 84001. D. C. Golden (Hernandez Engineering Inc.), Douglas Ming, and their colleagues at the NASA Johnson Space Center heated synthetic Fe-rich carbonates at 470°C and made faceted magnetites, which resembled those in ALH 84001. However Thomas-Keprta and colleagues presented many arguments against the formation of the Martian magnetites by thermal decomposition of carbonate. In particular they argued that the laboratory-grown magnetites grown by D. C. Golden and colleagues display cubo-octahedral faces whereas magnetites produced by one strain of bacteria and the presumptive Martian biogenic magnetites have six additional dodecahedral faces. (Thomas-Keprta and coworkers now call the second variety, "truncated hexa-octahedrons" but Buseck and colleagues note that this term is incorrect according to accepted crystallographic nomenclature.) Andrea Koziol (University of Dayton) and Adrian Brearley (University of New Mexico) also made nanometer-sized magnetites in the laboratory by briefly heating iron-magnesium carbonates to 470°C under different conditions. They did not grow any whisker-shaped crystals like those in ALH 84001 but argued that their faceted magnetites resembled the supposedly biogenic variety in ALH 84001 in many ways. Animated discussions at the conference suggested that arguments based on the crystal shapes of the meteoritic magnetites, both for and against biogenic origins, are not currently persuasive.

To help understand how the minerals in ALH 84001 formed and how they were modified by impact we have been studying a section of ALH 84001 using transmission and scanning electron microscopy. Our discoveries illuminate the origin of the magnetites in two ways.

A second oxide in ALH 84001 carbonate

Our first discovery was that magnetite is not the only oxide in the carbonate: a mineral called periclase, magnesium oxide (MgO), forms crystals in various locations in the carbonate and is most abundant in magnesium-rich carbonate. Like magnetite, the periclase forms 30-50 nanometer crystals, frequently associated with voids. Both types of crystals are shown in the images below.

Periclase and Magnetite in voids of ALH 84001 carbonate



(Adapted from Barber and Scott, 2002)

Scale bars are 100 nanometers.

In addition, aggregates of periclase crystals ~3 nanometers in size are oriented preferentially with respect to the carbonate crystal lattice, similar to what happens when calcite, calcium carbonate (CaCO_3), decomposes to lime, calcium oxide (CaO). To understand why these oxides are oriented preferentially in partly decomposed carbonate, we need to understand the crystal structures of these minerals.

Crystal structure

We found that the carbonate crystals in ALH 84001 have the structure of the mineral calcite (or the closely related mineral, dolomite, CaMgCO_3) and are at least 5 micrometers in size, very much larger than the crystals of magnetite or periclase. Although calcite, lime, and periclase have very different chemical compositions, their crystal structures can be related in simple ways by considering how the largest atoms, the oxygen atoms, are arranged in each structure. Lime and periclase both have the structure of sodium chloride (common salt), and this structure can be related to that of calcite by replacing the oxygen atoms in lime by CO_3 groups. The CO_3 groups are arranged in planes so that the oxygen atoms are close to the positions of oxygen atoms in the close-packed planes of oxygen in the lime or periclase structures. When calcite decomposes during heating to release carbon dioxide, it is therefore not surprising to find that the crystals of lime tend to form with their close-packed layers of oxygen atoms oriented nearly parallel to those in the parent carbonate crystal. We found the same relationship for the periclase crystals in magnesium-rich carbonate in ALH 84001. Such relationships are common in minerals and inorganic solids when one solid forms on the surface of, or within another that is structurally related. The orientation and location of the periclase crystals in ALH 84001 provide strong evidence that they formed inside the carbonate crystals as a result of thermal decomposition and loss of carbon dioxide. Since we found much evidence for localized shock melting of silicate minerals in ALH 84001, and there is additional evidence that the rock was heated by impact 4 Byr ago, it is probable that the carbonate was decomposed by impact heating, at this time, rather than by deep burial in the planet.

How magnetite crystals are oriented in the ALH 84001 carbonate

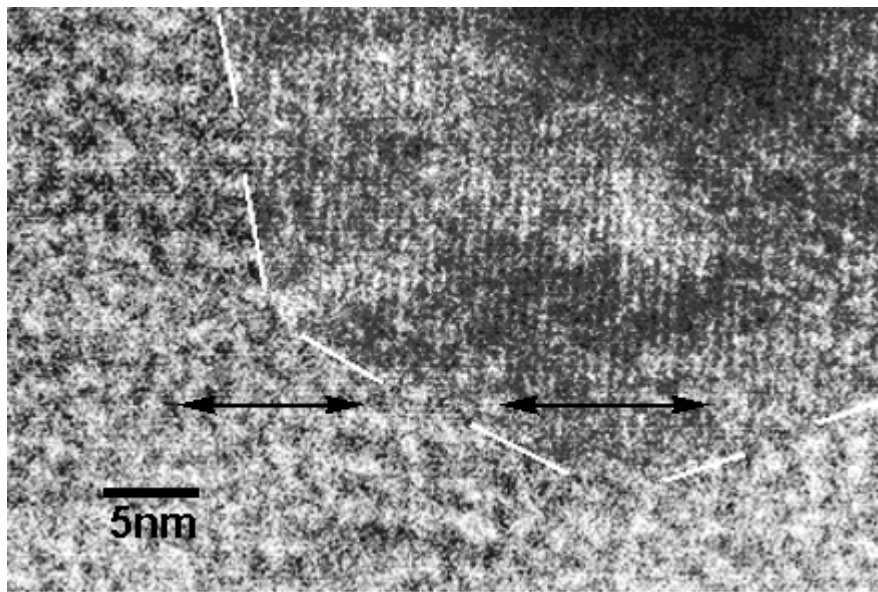
Our initial studies of periclase and magnetite crystals in ALH 84001 suggested that we should investigate in more detail the relative orientations of the magnetite and carbonate crystals. Although magnetite (Fe_3O_4) has more oxygen atoms per molecule than periclase (MgO) and lime (CaO), the oxygen atoms in all three minerals are arranged in almost identical close-packed layers. Thus any magnetites that form within the carbonate lattice following thermal

decomposition of carbonate may be crystallographically oriented. We therefore decided to look more carefully at the crystal lattices of adjacent magnetite and carbonate crystals.

We first showed that groups of magnetites in small voids and in microfractures are commonly oriented with respect to each other and the carbonate, so that their atomic lattices are aligned at their contacts. Mineralogists call this alignment epitaxy. John Bradley and colleagues found that the whisker-shaped magnetites exhibited epitaxy. An epitaxial relationship indicates abiogenic growth in or on the carbonate. We then studied the magnetites that were fully embedded in the carbonate crystal using techniques to image the lattices of both minerals, as individual magnetite crystals are too small to give good diffraction patterns. This required considerable patience and care because the carbonate crystal lattice is heated and easily damaged by the beam of electrons in the microscope.



David Barber at the helm of a JEOL 2010 analytical transmission electron microscope operating at 200 kV at the Hong Kong University of Science and Technology.



(Adapted from Barber and Scott, 2002)

Aligned atoms in carbonate and magnetite -- this electron microscope lattice image shows part of a faceted magnetite crystal (above the dashed line) which is embedded in a carbonate crystal. The horizontal lines (as shown by arrows) in the carbonate and the magnetite crystals are sets of atomic planes in the two crystals which have almost identical spacings and orientations. (The near vertical lines in the magnetite crystal are caused by a tiny mismatch in orientation and spacing between different atomic planes in the two minerals.) Such images show that the planes of oxygen atoms in the two minerals are closely aligned and that the magnetite crystal must have formed inside the carbonate crystal. The 5 nanometer scale bar is ~20 times the diameter of an oxygen atom.

We found that the embedded magnetite crystals give good lattice images whenever the carbonate crystal is aligned so that the electron beam is parallel to rows of atoms in the carbonate crystal. This finding implies a fully three-dimensional relationship between the two atomic structures, which is called topotaxy. But to prove it beyond doubt we had to repeat the exercise after turning the carbonate crystal and its embedded magnetite crystal to a new orientation relative to the electron beam. Invariably the first image showed good continuity of lattice planes across the magnetite-carbonate boundary, though with some distortion. The second image was usually inferior because of the cumulative electron damage to the carbonate crystal, despite the precautions taken to minimize heating and beam damage. Nevertheless, we were able to confirm that the second image also showed lattice continuity across the magnetite-carbonate boundary. Many but not all magnetites are oriented with their close-packed layers of oxygen atoms aligned with those in the carbonate, consistent with what we observed for periclase. This demonstrates that the embedded magnetite crystals formed within the carbonate crystal by diffusion of atoms and loss of carbon dioxide.

Implications for the supposedly biogenic magnetites

We surveyed all the different locations in carbonate where magnetite crystals occur and found that the diverse sizes, shapes, and abundances were consistent with the nucleation and growth of magnetite in carbonate. Magnetite, like periclase, nucleated on voids, microfractures, and other defects. The magnetites display all the features of precipitates that form in cooling crystalline solids when atoms can diffuse far enough for new crystals to grow but not far enough to reach the boundaries of the parent crystals. Small crystals that form under these conditions tend to have well-developed faces.

We could not identify the crystal faces of the topotactically oriented magnetites. Trying to infer the exact external shape of embedded nanocrystals from conventional electron microscope images is like trying to guess the shape of an object suspended in a glass of water from its silhouette. But we did find that magnetite crystals with well-developed external faces, like the supposedly biogenic crystals, occur as individual crystals within the carbonate and commonly

show topotactic orientations. Magnetites in the optically-opaque rim are crowded together and appear to be more irregular in shape, consistent with growth in a highly strained carbonate crystal.

These results are not consistent with those of Thomas-Keprta and colleagues who concluded that the supposedly biogenic magnetites are not preferentially oriented with respect to the carbonate lattice. They inferred that the presumptive biogenic magnetites are located in the opaque rims where they are surrounded by randomly oriented carbonate crystals as small as 10 nanometers across (cf. 4-100 nanometers for the magnetites). This would preclude a crystallographic relationship between the carbonate and magnetite lattices. However, we find that some of the magnetites in the opaque rim are preferentially oriented and that the adjacent carbonate usually consists of slightly misoriented regions ~100 nanometers in size. The strain fields in the carbonate crystal around the abundant magnetites appear to have interacted to produce this microstructure during magnetite growth. There was no evidence that the carbonate crystals increased in size during our experiments.

Some arguments that have been advanced against formation of magnetite by the thermal decomposition of carbonate

Several arguments have been offered against the formation of magnetites in ALH 84001 by thermal decomposition of carbonate and many were discussed at the March 2002 Lunar and Planetary Science Conference. Below we offer responses to these arguments.

1. Many magnetites are entirely embedded in carbonate and are not accompanied by voids contrary to what would be expected if the carbonate decomposed by simply breaking down into oxides and carbon dioxide.

Our response: Decomposition of even a pure carbonate mineral is no simple matter. In calcite, for example, there are no CaCO_3 molecules that simply break into CaO and CO_2 molecules as one might suppose. Even though carbonates have well-defined structures with specific sites for all atoms, they behave like well-regulated soups of charged atoms, vacancies, and defects that are all hopping around at speeds that depend on the temperature. So when calcium carbonate decomposes, calcium oxide and carbon dioxide can form at different sites and times. In the case of ALH 84001, our evidence for topotaxy and faceted voids shows that all species of atoms as well as vacancies could diffuse over hundreds of nanometers through the carbonate when the magnetite formed. Thus, voids and magnetite need not be closely associated.

2. Many experiments in which iron-magnesium carbonates were decomposed by heating have generated magnesium-rich magnetite not the pure magnetite observed in ALH 84001.

Our response: Decomposition of iron-magnesium carbonate is much more complex than decomposition of calcium carbonate because different oxides can form depending on the nature of the gas around the carbonate. Although there are some inconsistent reports in the literature, Andrea Koziol concluded at the March 2002 Lunar and Planetary Science Conference that in oxygen-rich environments magnesium-iron carbonates decompose to form magnesium-rich magnetite, but under oxygen-poor conditions, pure magnetite is formed.

3. Some magnetites in ALH 84001 appear to be enriched in aluminum and chromium relative to the carbonate, inconsistent with simple decomposition of carbonate.

Our response: The magnetites in ALH 84001 did not form by simple decomposition of carbonate crystals: the process was much more complicated. For a 100-nanometer sized magnetite crystal to have formed within a carbonate crystal, atoms must have diffused through the carbonate structure over distances of hundreds of nanometers. Atoms of magnesium and calcium would have diffused away from the construction site of the new magnetite crystal while iron atoms diffused towards it. Aluminum and chromium atoms fit better into the structure of magnetite than carbonate, so enrichments of these elements might be expected.

4. *Magnetites in the opaque rims are associated with the iron sulfide pyrrhotite, which appears too abundant to have formed by precipitation from carbonate.*

Our response: We did not find pyrrhotite: in our section, sulfide in the opaque rims appeared to be present as finely crystalline or possibly amorphous material. We cannot exclude the possibility that some sulfide precipitated from the fluid that generated carbonate before magnetite formed.

5. *Most experiments that have tried to reproduce the magnetite population in ALH 84001 by thermal decomposition of carbonate have failed in some regard. For example, experiments by Koziol and Brearley generated randomly oriented magnetite crystals.*

Our response: Differences between synthetic and Martian magnetites should be expected because the Martian carbonate was heated and may itself have crystallized during a large impact on Mars. We do not know the detailed thermal and shock history of ALH 84001 and even if we did it would be extremely difficult to simulate those conditions exactly in the lab. So we should not expect simple experiments to reproduce all of the features of the ALH 84001 magnetite.

6. *Since microorganisms can form magnetites oriented in chains, how do we know that they cannot orient magnetites on carbonate?*

Our response: Microorganisms can certainly orient magnetite crystals crystallographically within their cells, but not outside their cells. Minerals made outside cells by organisms are not well ordered, have wide ranges of grain sizes, and cannot be crystallographically oriented.

Shock heating of carbonate

We think that there is now abundant evidence that most and probably all of the magnetites in ALH 84001 formed because of shock heating of carbonate. Faceted magnetites resembling the supposedly biogenic magnetites are crystallographically oriented in the carbonate lattice and could not have formed inside bacteria. We infer that ALH 84001 magnetites differ from abiogenic terrestrial magnetites because terrestrial carbonates never experienced the unique impact history of ALH 84001.

If any magnetites with the sizes of the supposedly biogenic variety had been deposited in the ALH 84001 carbonate prior to the impact heating that caused oxide precipitation, they could not have retained their original properties. Even supposing that an earlier generation of magnetites were completely impervious to the shock wave that heated the carbonate above about 450°C and were totally immune to any reaction with the shock-heated or shock-melted carbonate [See [PSRD](#) article: [Shocked Carbonates May Spell N-O L-I-F-E in Martian Meteorite ALH 84001](#)], they would certainly have acted as seed crystals during subsequent cooling. Thus any magnetites deposited in the carbonate prior to impact heating would have been coated with new layers of magnetite up to tens of nanometers in thickness. Martian organisms cannot therefore be responsible for the size and shape of any magnetite crystal in the ALH 84001 carbonate.

The future of ALH 84001

Does this result mean that ALH 84001 will now return to obscurity? Absolutely not! Meteorites are cosmic gifts that keep on giving, and giving! It is still the oldest rock we have from any planet: it crystallized over 4.4 billion years ago. We have tiny lunar fragments with comparable ages that were extracted from breccias but we don't know why the ancient Martian crust should be so well preserved in ALH 84001 if the Moon and Mars suffered the same bombardment history. How were the carbonates in ALH 84001 formed? What was the intensity of the Martian

magnetic field when the magnetites cooled? How and where was ALH 84001 launched from on its journey from Mars to Earth? An ancient Martian rock is indeed a precious gift, even if it failed to bring evidence for extra-terrestrial life.

Additional Resources

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