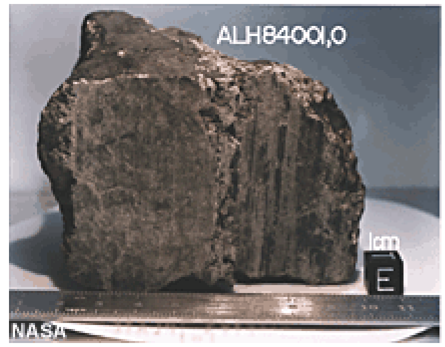
Hot Idea

October 30, 2007



Did an Impact Make the Mysterious Microscopic Magnetite Crystals in ALH 84001?

--- Tiny crystals of magnetite in Martian meteorite ALH 84001 might have been made when shock waves decomposed iron carbonate.

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Fervent debate swirls around microscopic crystals of magnetite (Fe_3O_4) in Martian meteorite ALH 84001. Some investigators suggest that the crystals are evidence of past life on Mars, citing magnetite crystals of similar chemical compositions and sizes made by magnetotactic bacteria on Earth. Others cite assorted experiments and observations to argue that the important little crystals formed entirely by non-biological processes, hence say nothing about life on Mars. One of those processes is the decomposition of iron carbonate (the mineral siderite), which occurs in ALH 84001. Researchers argue that heating this mineral causes it to decompose into magnetite and CO_2 gas. Experiments showing this were done by heating siderite and observing that it decomposed and formed magnetite, but nobody had shock-heated siderite to see if magnetite crystals formed. (Shock is a rapid, strong rise and fall in pressure. It happens under many circumstances, including meteorite impacts.)

The lack of shock experiments has been solved by Mary Sue Bell (University of Houston and Jacobs Engineering). She experimentally shocked samples of siderite at the Experimental Impact Laboratory at the Johnson Space Center. She shows that magnetite crystals of the right size and composition formed when samples were shocked to 49 GPa (about 500,000 times the pressure at the Earth's surface). This is more evidence for a non-biological origin for the magnetite crystals in ALH 84001 and is consistent with what we know about the impact history of the rock. There seems to be growing evidence against a biological origin, but don't expect these results to completely settle the debate!

Reference:

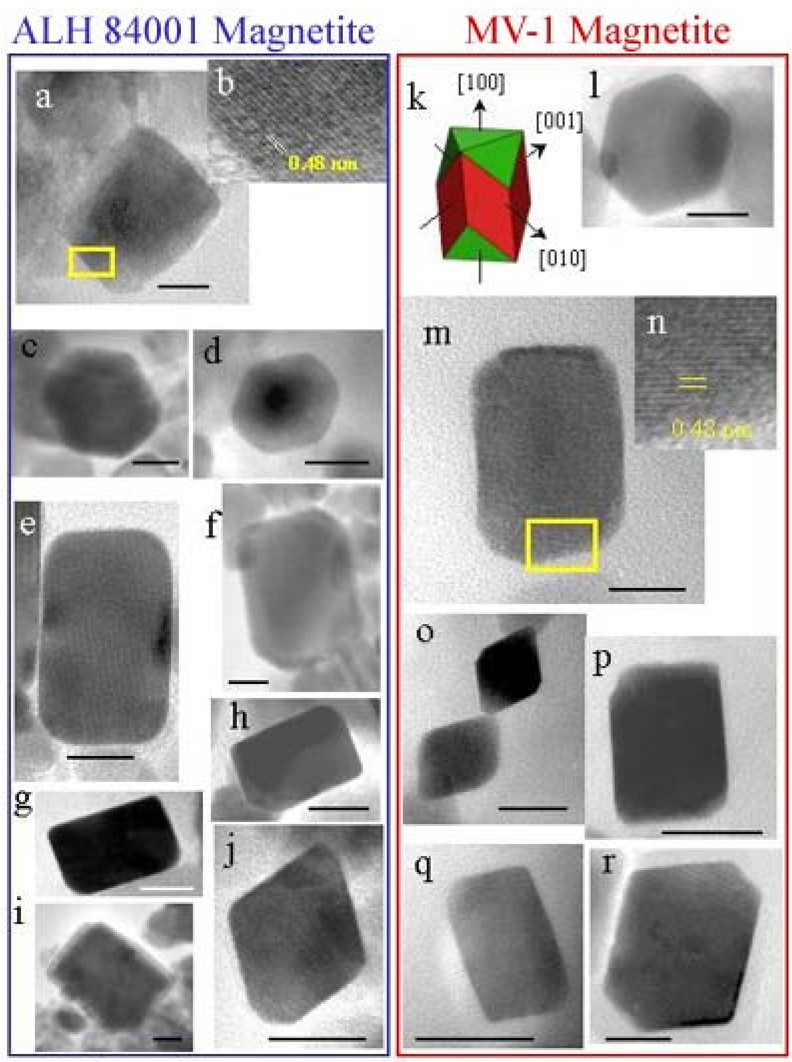
- Bell, M. S. (2007) Experimental Shock Decomposition of Siderite and the Origin of Magnetite in ALH 84001. *Meteoritics and Planetary Science*, v. 42, p. 935-949.

PSRDpresents: Did an Impact Make the Mysterious Microscopic Magnetite Crystals in ALH 84001? --Short Slide Summary (with accompanying notes).

Tiny Crystals, Big Arguments

A group led by David McKay at the Johnson Space Center, with co-workers elsewhere, made the startling claim in 1996 that there was evidence for fossil life in Martian meteorite ALH 84001 (see our first **PSRD** article: Life on Mars?). The evidence they cited has taken quite a beating during the past decade as scientists enthusiastically tested each argument (that is, they tried to prove the hypothesis wrong). The one line of evidence still open is the presence of tiny crystals of compositionally-pure magnetite. A vociferous debate has been raging about their origin. On one side is the McKay group, with the magnetite studies spearheaded by Kathy Thomas-Keprta. On the other side is almost everyone else who has studied the rock (plus some who haven't!).

Kathy Thomas-Keprta and her colleagues cite five reasons for concluding that at least a subset of the magnetite crystals in ALH 84001 formed inside microorganisms. These include their shapes (mostly prisms), sizes (4-100 nanometers), and their chemical purity (essentially pure iron oxides). Their arguments stem from the properties of magnetite grains produced by what biologists call magnetotactic bacteria on Earth.

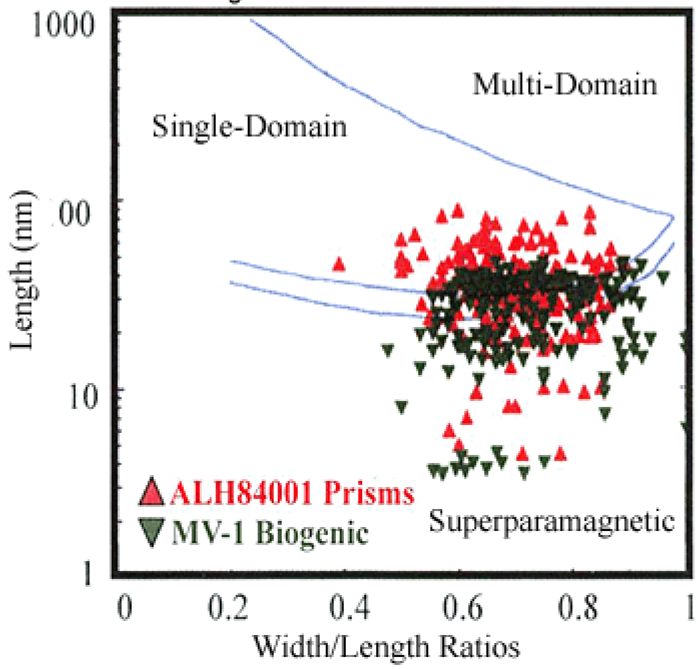


Scale bars=20 nm

(From Thomas-Keprta *et al.*, 2000, *Geochim. et Cosmo. Acta*, v. 64, p. 4056.)

Kathy Thomas-Keprta and her colleagues separated magnetite crystals from the ALH 84001 carbonate globules. Many have well-formed crystal shapes like those in the electron microscope images shown on the left. They look a lot like magnetites formed by terrestrial magnetotactic bacteria, such as the bacteria designated MV-1, shown on the right.

Magnetite crystals in ALH 84001 compared to Magnetites from Bacteria on Earth

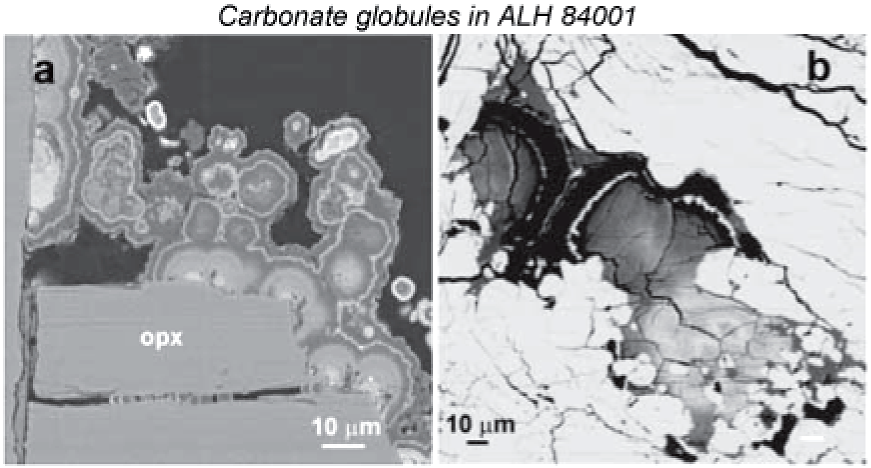


(From Thomas-Keprta *et al.*, 2000, *Geochim. et Cosmo. Acta*, v. 64, p. 4063.)

Graph of magnetite sizes in ALH 84001 and in terrestrial magnetotactic bacteria. The overlap of the data shows that many of the small magnetite crystals in the meteorite have similar sizes to those made by terrestrial bacteria, such as strain MV-1.

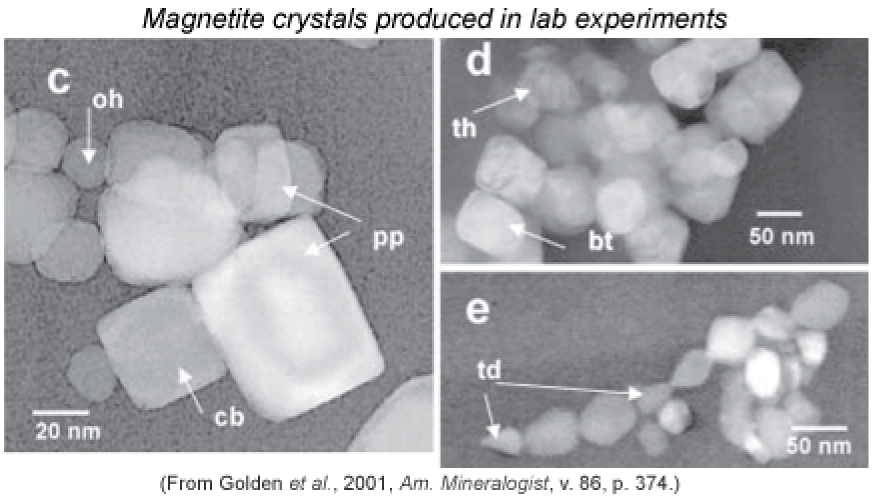
Although the similarities in shape, size, and composition of magnetite crystals in ALH 84001 and terrestrial magnetite-producing bacteria seem convincing, most cosmochemists and astrobiologists considered the evidence circumstantial. Similarity does not prove origin, they argued, and proposed alternative ways of producing the magnetite crystals. The most popular non-biological origin involves heating inorganically-produced iron carbonate to form magnetite and carbon dioxide gas. One interesting set of experiments was done at the Johnson Space Center by D. C. Golden and his colleagues. Golden formed globules of carbonate minerals by precipitation from solutions of salty hot water (see the image on the left, below). They resembled those in ALH 84001 (see image on the right, below). He then heated the products and showed that a variety of magnetite crystals formed from the iron carbonate minerals in the laboratory products.

Carbonate globules produced in lab experiments compared to Carbonate globules in ALH 84001

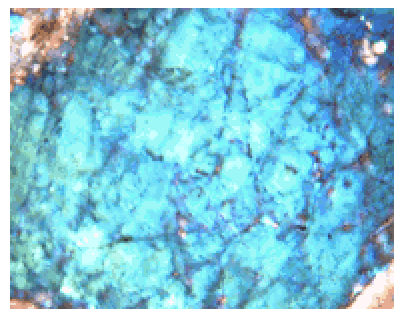


(From Golden *et al.*, 2001, *Am. Mineralogist*, v. 86, p. 373.)

These scanning electron microscope images show the carbonate globules produced by precipitation from a hot (150 Celsius) water solution (LEFT), compared to similar carbonate globules in ALH 84001 (RIGHT).



These are transmission electron microscope images (in reverse contrast) of magnetite crystals formed by heat-treating chemically-zoned carbonate globules made in D.C. Golden's laboratory at the Johnson Space Center. Image c shows a variety of shapes: parallelepipeds (pp), cubes (cb), and octahedral (oh). Image d shows tooth-shaped (th) and bullet-shaped (bt) grains of magnetite. Image e shows a chain of small magnetite crystals with tear-drop (td) shapes.



Shock damaged pyroxene crystal from ALH 84001 in the polarizing light microsope. Image credit: Edward Scott (University of Hawaii.)

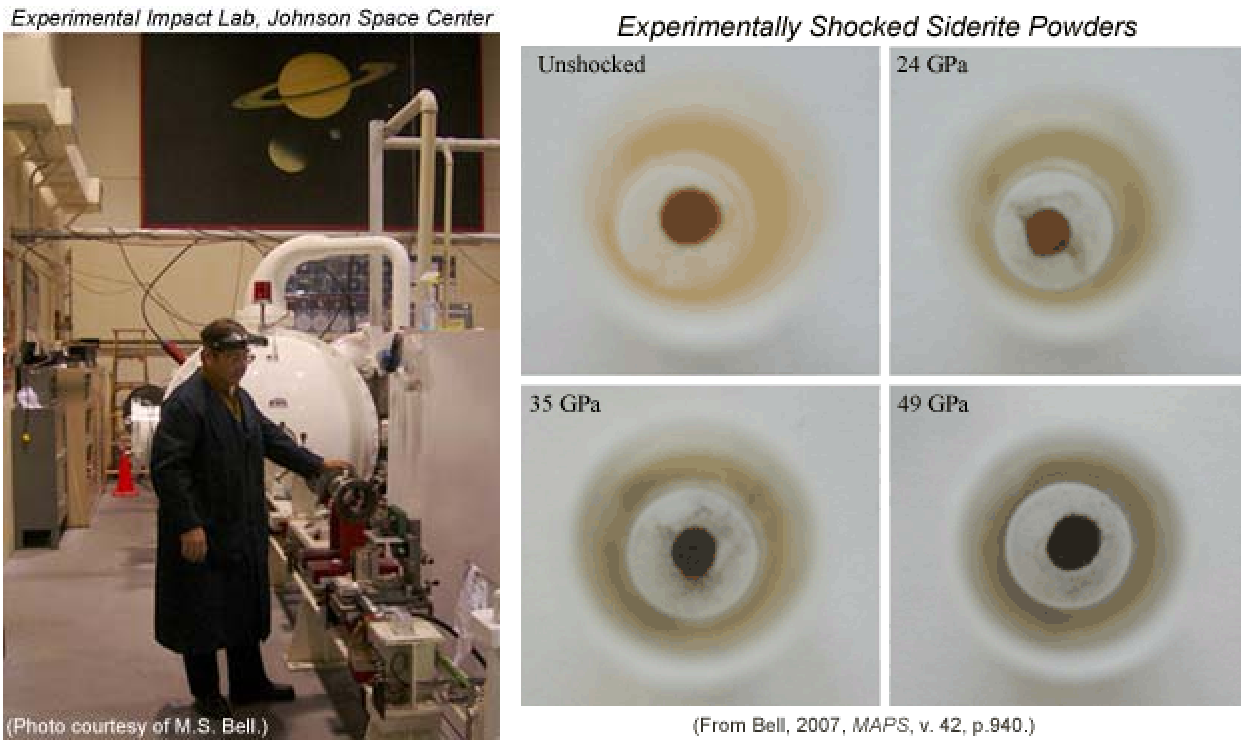
Other investigators presented evidence that the magnetite in ALH 84001 formed by carbonate decomposition. For example, see **PSRD** article: [Resolution of a Big Argument About Tiny Magnetic Minerals in Martian Meteorite]().

These results convinced many researchers that tiny magnetite crystals could form when impacts heated the rock and caused carbonate minerals to decompose, but none used an actual shock experiment to produce magnetite from siderite. This is an important gap because ALH 84001 is strongly shocked. In fact, Allan Treiman (Lunar and Planetary Institute, Houston) has shown that the rock experienced several separate shock events. This is not surprising for an old rock (it initially crystallized 4.5 billion years ago) because planetary surfaces were severely bombarded until 3.8 or 3.9 billion years ago. Everyone agrees that the rock formed in a large body of magma trapped deep in the Martian crust. It was excavated at some point to a location near the surface where water evaporated and precipitated carbonate minerals, including siderite, along grain boundaries. The rock was shocked after that event, causing assorted deformation of the carbonates, possibly including decomposition of the siderite.

Shocking Rocks in the Lab

All that makes a detailed story of shock events, yet there have been no shock experiments done to show that shock and the instantaneous heating accompanying it can cause decomposition of siderite. Mary Sue Bell has fixed that problem. She obtained unshocked siderite from Natural Copper Lake in Nova Scotia (see photo), and thoroughly characterized it with electron microprobe analysis and transmission electron microscopy. Because elements such as magnesium, manganese, and calcium readily substitute for iron in siderite, it is rarely found as pure $FeCO_3$. Bell demonstrates this through x-ray imaging in the electron microprobe. The siderite is composed mostly of iron, but also contains significant amounts of magnesium and calcium. The composition is also not uniform throughout the mineral grains.

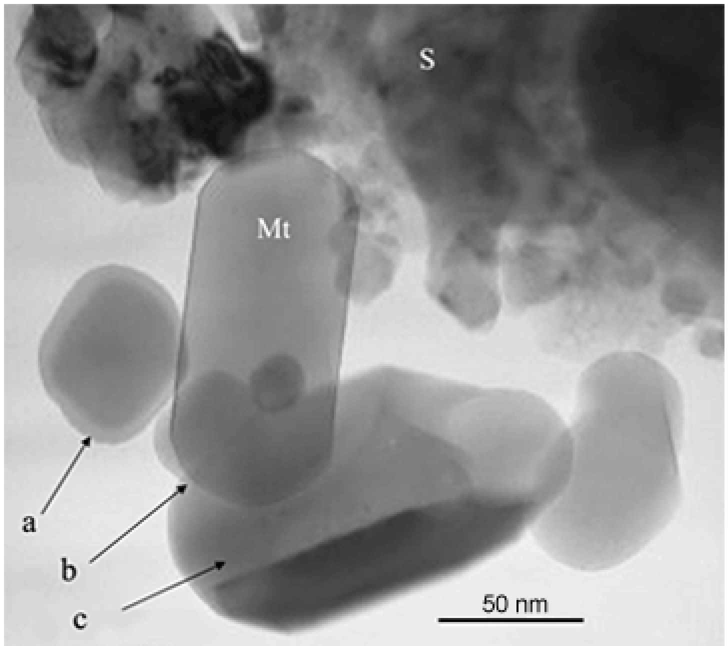
Bell crushed the siderite sample in alcohol to prevent oxidation, and sieved it to obtain a size fraction ranging from 120 to 250 micrometers. She took small (70 milligram) samples of the crushed rock and packed them into tungsten-alloy holders that contained no iron, and placed them in the experimental shock apparatus. (see photo below, left). The siderite powder samples were shocked at pressures ranging from 24 to 49 GPa in a chamber containing carbon dioxide to simulate conditions at the Martian surface. The shock effects are obvious even just looking at the samples in colorless vials (see photo below, right).



[LEFT] Jerry Hanes is shown loading "the gun" in JSC's Impact Laboratory. This is where the siderite powders were shocked to specific pressures. [RIGHT] The original, unshocked siderite powder is reddish brown, but became darker at progressively higher shock pressures.

The shock effects are more dramatic when given a closer look with an electron microscope. Small magnetite crystals are present when shocked to 49 GPa, indicating decomposition of some of the siderite to magnetite. The magnetite crystals are small and resemble the prism-shaped crystals in ALH 84001, although they are generally larger than those in the meteorite. The magnetite crystals contain up to 19 mole percent magnesium, but some contain no detectable magnesium.

Shocked Siderite from the Lab Experiment at 49 GPa



(From Bell, 2007, *MAPS*, v. 42, p.943.)

This transmission electron microscope image shows the transformation of siderite to magnetite when shocked to 49 GPa pressure. In the upper right area, labeled "S", is siderite containing nucleating crystals of magnetite. The other crystals in this image are magnetites of different shapes. Arrow "a" points to an equant crystal, arrow "b" points to an euhedral elongated crystal, and arrow "c" points to a subhedral elongated magnetite crystal.

Will the Debate Go On for Another Decade?

Thomas-Keprta and her colleagues call attention to the purity of the magnetite in marshalling evidence for a biogenic origin. Terrestrial magnetite formed by bacteria are essentially pure Fe_3O_4. However, there seems to be disagreement about how pure the magnetite crystals are in ALH 84001. For example, D. C. Golden and colleagues at the Johnson Space Center argue that the magnetite crystals in the meteorite are not pure iron oxide. They found, using the same transmission electron microscopy and procedures used by Thomas-Keprta, that magnetite in ALH 84001 contains up to 3 mole percent magnesium, although they also found that many contain no detectable magnesium. (Much of the hard-fought debate about the origin of magnetite in ALH 84001 involves different groups of investigators at the Johnson Space Center. I wonder if that puts a damper on the annual office Christmas party!)

The compositions and sizes of the magnetite crystals produced in Bell's shock experiments may not match perfectly with those in ALH 84001, but they do show unequivocally that shock can produce magnetite by decomposition of siderite. Thomas-Keprta and her colleagues have argued in the past that magnetite in ALH 84001 formed by more than one process, one of which was biogenic. They do not deny that the rock was shocked and that the shock and other thermal events could cause decomposition of siderite. But, they argue, the tiny, prismatic, pure magnetite crystals formed by microscopic organisms living in water flowing along cracks in rock.

Figuring all this out is clearly a tricky business. Searching definitively for life on Mars requires samples without such a complicated history. Such samples might be found by carefully examining promising regions on Mars, obtaining samples, and bringing them back to Earth. A Mars sample return mission might be launched as early as 2018. Maybe after detailed study of those samples everyone will agree on whether the rocks and soil returned contain evidence for present or past life on Mars.

Additional Resources

LINKS OPEN IN A NEW WINDOW.

- **PSRDpresents:** Did an Impact Make the Mysterious Microscopic Magnetite Crystals in ALH 84001? --Short Slide Summary (with accompanying notes).

- Bell, M. S. (2007) Experimental Shock Decomposition of Siderite and the Origin of Magnetite in ALH 84001. *Meteoritics and Planetary Science*, v. 42, p. 935-949.
- Golden, D. C., Ming, D. W., Schwandt, C. S., Lauer Jr., H. V., Socki, R. A., Morris, R. V., Lofgren, G. E., and McKay, G. A. (2001) A Simple Inorganic Process for Formation of Carbonates, Magnetite, and Sulfides in Martian Meteorite ALH84001. *American Mineralogist*, v. 86, p. 370-375.
- Scott, E. R. D. and Barber, D. J. (May, 2002) Resolution of a Big Argument About Tiny Magnetic Minerals in Martian Meteorite. *Planetary Science Research Discoveries.* http://www.psrd.hawaii.edu/May02/ALH84001magnetite.html
- Taylor, G. J. (October, 1996) Life on Mars? *Planetary Science Research Discoveries.* http://www.psrd.hawaii.edu/ Oct96/LifeonMars.html
- Thomas-Keprta, K. L., Bazylinski, D. A., Kirschvink, J. L., Clemett, S. J., McKay, D. S., Wentworth, S. J., Vali, H., Gibson Jr., E. K., and Romanek, C. S. (2000) Elongated Prismatic Magnetite Crystals in ALH84001 Carbonate Globules: Potential Martian Magnetofossils. *Geochimica et Cosmochimica Acta*, v. 64, p. 4049-4081.

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