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Hot Idea posted May 22, 1997

Low-temperature Origin of Carbonates Consistent with Life in ALH84001

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Much of the evidence for fossil life in martian meteorite ALH84001 is contained in globules, plates, and veins of chemically-complex carbonate minerals. For life to have existed in this rock, the carbonates must have formed at a temperature low enough to ensure survival, probably less than about 150 ^{o}C. Two recent papers in the same issue of the journal *Science* suggest that the carbonates formed at sufficiently low temperatures to permit life. The interpretations stem from measurements of the magnetic properties of minerals in ALH84001 (Kirschvink and others, 1997) and from the chemical and isotopic compositions of carbonates (Valley and others, 1997). Science is rarely so clear cut, of course, and not all data agree with a low-temperature origin. For example, see the **PSR Discoveries** article by Edward Scott about shock effects in ALH84001.

References:

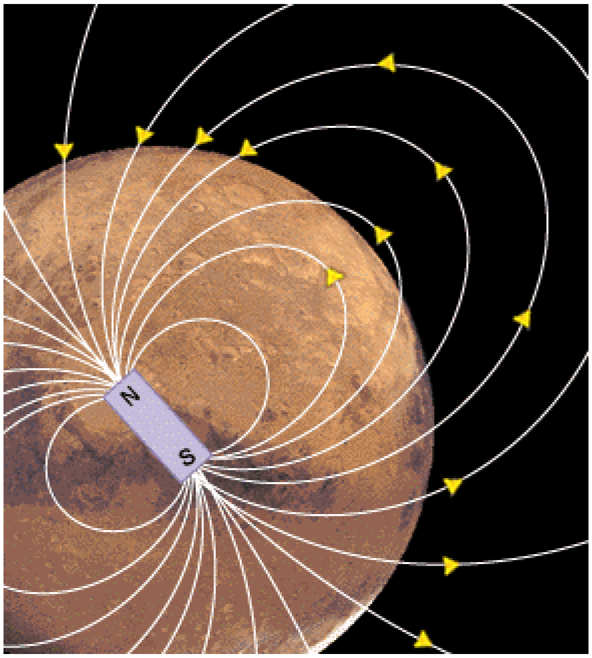
Kirschvink, J. L., A. T. Maine, and H. Vali, 1997, Paleomagnetic evidence of a low-temperature origin of carbonate in the martian meteorite ALH84001, *Science*, vol. 276, p. 1629-1633.

Valley, J. W., J. M. Eiler, C. M. Graham, E. K. Gibson, C. S. Romanek, and E.M. Stolper, 1997, Low-temperature carbonate concretions in the martian meteorite ALH84001: Evidence from stable isotopes and mineralogy, *Science*, vol 275, p. 1633-1638.

Rotated Magnets

The Earth has a substantial magnetic field, a feature that protects us from radiation by substantial solar flares. In fact, the Earth's magnetic field behaves as if there were a huge bar magnet inside the planet. The field arises from the motions inside the metallic, liquid outer core of the Earth; the motions are driven by the Earth's rotation and heat flowing from the inner, solid core. Other planets also have magnetic fields, but at present the fields of Mercury, the Moon, and Mars are quite weak, less than 1% of Earth's field. However, their magnetic fields might have been stronger in the past, and knowing how strong would be helpful in understanding the composition of their cores, how long the cores were molten, and the origin of planetary magnetic fields. But how can we measure a past magnetic field? The answer is simple: many rocks record the strength and direction of the magnetic field at the time of their formation.

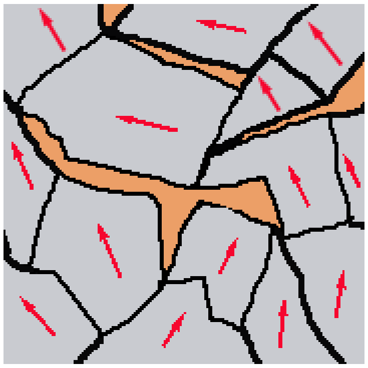
As hikers know, some minerals line up with the Earth's magnetic field, allowing them to determine which way they are walking. The original magnets were flakes of the mineral magnetite, Fe_3O_4, which is naturally magnetic. At high temperatures, above 580 ^{o}C, grains of magnetite are not magnetic. Thus, when, for example, a lava flow or other igneous rock solidfies, magnetite forms and is held in place by the other minerals in the solid rock, but is not magnetized until the temperature has fallen to 580 ^{o}C. At that temperature, called the Curie temperature, the magnetite becomes magnetized in the direction of the field at that time and place. The rock has recorded a lot of information about the magnetic field, and as long as the rock is not heated above the Curie point or is not chemically rotted by water and air, the record is preserved. Besides iron oxide, some iron sulfides also record the magnetic direction.



Mars might have had a magnetic field similar to Earth's, perhaps formed by fluids moving inside a molten core. If so, it would be as if a gigantic bar magnet sat inside the planet. In the diagram, the arrows represent the direction of the local magnetic field on the surface of Mars. (PSR Discoveries graphic.)

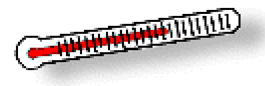
Magnetic directions in ALH84001

Joseph Kirschvink and his colleagues at the California Institute of Technology decided to measure the magnetic properties of a very small sample taken from an area of ALH84001 where the pyroxene crystals had been broken up. Their sample had a mass of only about 20 milligrams, yet they were able to separate grains and measure the strength and direction of the magnetism. The pyroxene fragments contained small inclusions of iron sulfide (FeS), which is probably the main carrier of the magnetism. Magnetic measurements are done in a special laboratory that is shielded from the Earth's strong field by about six tons of steel plates buried in the walls of the laboratory, and some high-tech devices closer to the magnetometer. It is like protecting samples from contamination during chemical analysis.



Arrows indicate direction of magnetic field.
Gray grains are pyroxene.
Orange grains are carbonate.

Although the investigators have measured only a few grains so far, the results are startling, and shown schematically on the left. They found that the grains differed greatly in the direction of magnetization. So instead of all pointing in the same direction, they pointed in a wide range of directions, as indicated by the arrows. When the rock first crystallized, all parts would have been magnetically aligned. When the rock was damaged by an impact, some of the fragments rotated, causing separate grains to appear to line up in different directions. (PSR Discoveries graphic.)



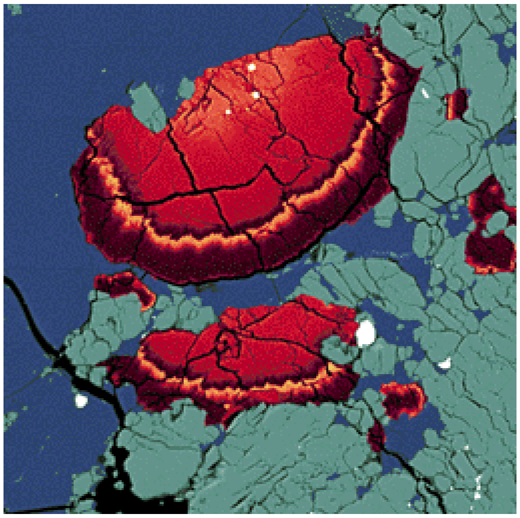
The important point for understanding the temperature of formation of the carbonates is that they fill up the spaces in between the pyroxene fragments, so were deposited after the fragmentation. Most important, if the carbonates had come in hot, above the Curie temperature for iron sulfide, then the original magnetization would have been erased, and the magnetic minerals would have recorded the field at the time they cooled, and they all would have been aligned in the same direction. Since they are aligned every which way, the carbonate must have been no hotter than the Curie temperature, about 325 ^{o}C for FeS. This is still too hot for life to have existed, but it is an upper limit to how hot the rock could have been heated--the temperature was most likely much lower. Detailed analysis of their magnetic data lead Kirschvink and his colleagues to conclude that the magnetic grains were not heated above 110 ^{o}C, within the range in which life can exist. They suspect that further measurements may suggest a temperature as low as 40 ^{o}C.

The strength of the martian magnetic field

The Caltech magnetic measurements demonstrate the importance of ALH84001 beyond the issue of life on Mars. The strength of the field Kirschvink and coworkers measured is surprisingly high, suggesting that the magnetic field on Mars 4 to 4.5 billion years ago was approximately as strong as the magnetic field of the Earth now. This means that it is likely that Mars had a liquid, metallic (or at least electrically conducting) core very early in its history. And, because the younger SNC meteorites have only weak magnetization, the magnetic field decreased with time, perhaps because the core crystallized. We need many more measurements before a detailed picture of the evolution of the martian core and magnetic field are known with certainty, but this first glimpse is tantalizing.

Minerals and isotopes suggest low temperatures

The minerals present in a rock, the compositions and compositional homogeneity (uniformity) of those minerals, and the relative abundances of the oxygen isotopes in them are like little thermometers planted inside the rock. John Valley, with collaborators at his institution (University of Wisconsin, Madison), Caltech, the University of Edinburgh in Scotland, and the University of Georgia, tried to read the little thermometers in ALH84001.



When viewed in an electron microscope, it is obvious that the carbonate globules are complicated. This photograph is a colorized image of the intensity of electrons bounced back from a polished surface of a sample of ALH 84001. The colors represent different minerals. Green is orthopyroxene (the silicate with iron and magnesium), blue is glassy plagioclase feldspar, and the various shades of red and orange are carbonate minerals with a range in chemical composition. (Photo courtesy of Ralph Harvey, Case Western Reserve University.)

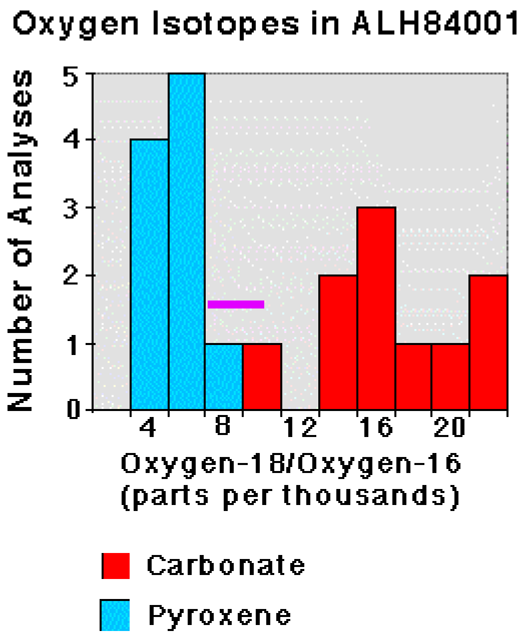
Valley and colleagues paid special attention to the amazing complexity of the carbonates in the meteorite. To use those little thermometers inside rocks, the minerals must be in chemical equilibrium. This means that the minerals have reached an agreement with one another, an agreement impelled by the laws of thermodynamics, about how to distribute the elements composing them. If the minerals can be shown to be in equilibrium, then a vast storehouse of experimental data can be tapped to estimate the temperature of formation. Unfortunately, the carbonate minerals are not in equilibrium, making estimates of the temperature very difficult. As Valley and co-workers point out, carbonate minerals formed at low temperatures in shallow seas on Earth do not appear to be in equilibrium, and if you tried to calculate their temperature of formation you would conclude that the oceans are at a temperature of 500 ^{o}C!

Valley and colleagues analyzed the compositions of the carbonates, and agree with Ralph Harvey (Case Western Reserve University) and Harry Y. McSween (University of Tennessee) about the compositional diversity of the carbonate globules and plates. However, they argue strongly that Harvey and McSween's conclusion that the carbonates formed at high tempertures (above 650 ^{o}C) is incorrect. Besides the problem of lack of equilibrium, Valley points out that if the temperature were high for even relatively short times, only days or even minutes, the minerals would have homogenized because elements are fairly mobile at high temperatures. Even more damaging, high temperatures would have caused assorted chemical reactions to take place, producing new minerals that are not observed in ALH84001.

Low-temperature Features

The chemical inhomogeneity of the carbonates is more consistent with a low-temperature origin. Elements move slower at low temperatures than at high temperatures, so minerals do not homogenize easily. Estimating the temperature precisely is still difficult, because of the lack of equilibrium. Nevertheless, a good guess can be made from the abundances of oxygen isotopes, specifically oxygen-16 and oxygen-18. The ratio of these isotopes is dependent on the formation temperature of different minerals.

Valley and his associates measured the abundances of oxygen isotopes in ALH84001 carbonates using an ion microprobe, a high-tech device that can measure tiny quantities in tiny spots (about 30 micrometers across) on polished slabs of a rock. This gets around the extreme difficulty of physically separating small grains and analyzing by other techniques. It raises other analytical difficulties, but these seem to be manageable.



The data obtained by Valley and co-workers are shown in the graph above. The oxygen isotope data are expressed as the amount of deviation of the ratio of O-18 to O-16 compared to a standard, almost always mean Earth ocean water. The important point is that the pyroxene has a low value of O-18/O-16, but the carbonates are higher, and much more scattered. If the pyroxene were in equilibrium with carbonate at a high temperature, as Harvey and McSween have argued, then the carbonate points should be in the range given by the purple horizontal bar, around 7 or 8 parts per thousands. Instead, the carbonate points lie far to the right of this range, consistent with formation at low temperature. (The ratio of oxygen isotopes is never exactly the same in co-existing minerals in a rock, even if they are in chemical equilibrium, mostly because the lighter isotope, oxygen-16, moves more readily than the heavier one. At high temperatures, the difference in their masses is less important than at lower temperatures, so the ratio is closer in co-existing minerals. However, at low temperature, the difference in the rates at which oxygen-18 and oxygen-16 move becomes more pronounced, leading to larger differences between minerals.)

Although they cannot estimate the temperature precisely because of the lack of equilibrium, the similarity to carbonates formed at low temperature (certainly less than 300 ^{o}C) on Earth leads Valley and his associates to conclude that the carbonates in martian meteorite ALH84001 formed at relatively low temperatures, too. Clearly, more work is needed to pin down the temperature more precisely-300 ^{o}C is too high for life to have existed.

Editor's note: The temperature at which the carbonates in ALH84001 formed is one of the most hotly debated issues about the evidence for fossils in the meteorite. For an opposing view, see **PSR Discoveries** article Shocked Carbonates may Spell N-o L-i-f-e in Martian Meteorite ALH84001 posted on May 22, 1997.

Additional Resources

Kirschvink, J. L., A. T. Maine, and H. Vali, 1997, Paleomagnetic evidence of a low-temperature origin of carbonate in the martian meteorite ALH84001, *Science*, vol. 276, p. 1629-1633.

Valley, J. W., J. M. Eiler, C. M. Graham, E. K. Gibson, C. S. Romanek, and E.M. Stolper, 1997, Low-temperature carbonate concretions in the martian meteorite ALH84001: Evidence from stable isotopes and mineralogy, *Science*, vol 275, p. 1633-1638.

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