

#### **Hot Idea**

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# **Liquid Water on Mars: The Story from Meteorites**

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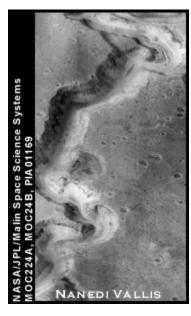
Two studies shed light on the nature and timing of alteration by water of rocks from Mars. One is an experimental study of the alteration of a rock similar to Martian meteorites, conducted by Leslie Baker, Deborah Agenbroad, and Scott Wood (University of Idaho). They exposed crushed pieces of terrestrial lava flows to water at 23 °C and 75 °C and normal atmospheric pressure, and to hot water at 200 °C to 400 °C and a pressure 1000 times normal atmospheric to see what minerals would form. On the basis of a detailed comparison between the experimental products and the Martian meteorites Baker and colleagues conclude that the rocks from which Martian meteorites derived were intermittently exposed to water or water vapor; they were not exposed for a long time to large volumes of water. In an independent study, a team led by Tim Swindle (University of Arizona) tried to determine the time of formation of a reddish-brown alteration product in the Martian meteorite Lafayette. This meteorite appears to have formed from magma 1.3 billion years ago, but the rusty-looking weathering product, a mixture of clay minerals, iron oxide, and iron hydride, formed long after the original rock had crystallized. Although the precise time is not pinned down, their measurements indicate formation during the past 650 million years. Taken together, these studies suggest that water flowed intermittently on the surface of Mars during the past 650 million years.

#### References:

Baker, L. L., Agenbroad, D. J., and Wood, S. A., 2000, Experimental hydrothermal alteration of a martian analog basalt: Implications for martian meteorities. *Meteoritics and Planetary Science*, vol. 35, p. 31-38.

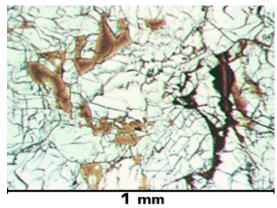
Swindle, T. D., Treiman, A. H., Lindstrom, D. J., Burkland, M. K., Cohen, B. A., Grier, J. A., Li, B., and Olson, E. K., 2000, Noble gases in iddingsite from the Lafayette meteorite: Evidence for liquid water on Mars in the last few hundred million years. *Meteoritics and Planetary Science*, vol. 35, p. 107-115.

#### **Wet Mars and Altered Meteorites**

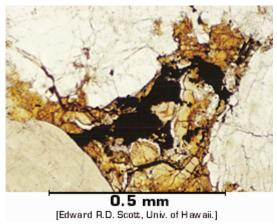


Volcanoes and vast lava plains form much of the bedrock on the surface of Mars. No doubt other igneous rocks reside beneath the rusty surface. However, the ground is cut by vast dendritic networks and huge channels that appear to have been carved by flowing water, leading scientists to conclude that at least in the past, liquid water was abundant on Mars. [See, for example, the image at left of Nanedi Vallis.] There is even some evidence that an ocean once existed in the Northern Hemisphere of Mars. This clement period in Martian history is thought to have occurred over three billion years ago. Martian meteorites also show evidence that liquid water flowed through them; the evidence is in the form of alteration products (minerals that formed at low temperature after creation of the original rock). However, the Martian meteorites are relatively young: all but one is 1.3 billion years old, or younger. The alteration products had to have something to alter, so they must have formed during the past 1.3 billion years, long after the suspected wet and warm climate on Mars had changed to the dry, cold conditions found today. How recently did the alteration minerals form? How much water was required to make the alteration products? How hot was the water? These are the questions Baker, Swindle, and their colleagues are trying to answer.

Martian meteorites possess an interesting, though complicated, array of alteration products. One type of Martian meteorite, the shergottites, are much like terrestrial <u>basalts</u>, and formed in lava flows. They consist mostly of the minerals <u>plagioclase feldspar</u> and <u>pyroxene</u>, but contain patches and veins of calcium carbonate and calcium sulfate, the alteration products. The nakhlites are quite different in composition. They are made mostly of pyroxene and <u>olivine</u>, with only a small amount of feldspar. Alteration products include calcium carbonate (like chalk) and calcium sulfate, sodium chloride (table salt), and iddingsite, a rust-colored mixture of clay minerals, iron oxide, and iron hydride.







Alteration products in two meteorites from Mars, Lafayette (left) and ALH 84001 (right). Lafayette has prominent occurrences of rusty-brown veins that are a mixture of clay minerals, iron oxide, and iron hydride. ALH 84001 is famous for its complicated globules of (brownish) carbonate minerals, in which the very controversial evidence for fossil

The only very ancient Martian meteorite is ALH 84001, which formed more than 4 billion years ago. It is composed almost entirely of pyroxene, but is decorated with tiny globules of carbonate minerals. The meteorite has been at the center of a controversy concerning the evidence for fossil life in it, and the carbonate globules are at the hub of that argument. Several ideas for the origin of the globules have been proposed, and estimates for the temperature at which they formed range from about 0 °C to 800 °C. Now there's a disagreement! It is also an opportunity to explore carbonate formation experimentally, and that is what Leslie Baker and her colleagues did.

#### **Martian or Terrestrial Weathering?**

There is absolutely no doubt that some of the alteration products formed on Mars. Allan Treiman (Lunar and Planetary Institute, Houston) and his colleagues reported the most dramatic example in 1993. While studying the nakhlite Lafayette they found that the rusty alteration product was truncated by the fusion crust, the melted zone on the outside of a meteorite that formed when the rock blazed through the Earth's atmosphere. Furthermore, the rusty veins are depleted in sulfur, chlorine, and phosphorus near the fusion crust. These elements are easily lost by heating. These observations indicate that the rusty veins must have been present when the meteorite hit the Earth's atmosphere.

On the other hand, it is not clear that *all* alteration products formed on Mars. Most of the Martian meteorites have been found on Earth, rather than observed to fall and picked up immediately. They could have weathered on Earth. Even the observed falls might be weathered somewhat. Thus, several researchers are trying to develop criteria to distinguish Martian from terrestrial weathering. Nevertheless, some of the products clearly formed on Mars and they may contain information about the Martian climate.

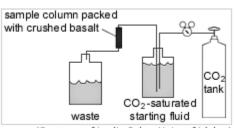
### **Soaking Rocks**

life was found.

In a nutshell, Leslie Baker and her colleagues put pieces of rock into little buckets of water. They chose a basalt from the Columbia River plateau for their experiments. The composition was not an exact match for Martian meteorites, but had similar levels of iron oxide, an important constituent when considering how weathering takes place. They crushed pieces of basalt and, for the high temperature experiments, ground it to a powder. The samples were then cleaned in an ultrasonic cleaner in dilute hydrochloric acid and rinsed in pure water to be sure pre-existing terrestrial weathering products were removed. Before placing a sample into the experimental apparatus, Baker sterilized it with hydrogen peroxide to prevent, as she writes, "an inadvertent life-on-Mars experiment."

They ran two sets of experiments, one at low temperature (23 °C and 75 °C) and another at high temperature (200 °C and 400 °C). The

low temperature experiments were done in an apparatus in which carbon dioxide gas (the main constituent of the thin Martian atmosphere) forced water through a sample container packed with the crushed basalt. The sample container was held at 23 °C or 75 °C by wrapping it in heating tape, sort of an electric blanket. The water that left the sample container was saved for analysis. The low-temperature experiments were run for four to seven days.





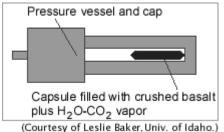
The diagram above shows the experimental set up used by Leslie Baker and her colleagues, and the photograph on the right is the actual apparatus. Carbon dioxide gas flows from the grey tank into a large bottle of water, which becomes saturated with carbon dioxide (starting fluid.) The water leaves the container and flows through the sample column, which contains crushed basalt. Wastewater flows down into the second bottle.





Research assistant Becca Carpenter prepares a sample holder for a new set of experiments.

The high temperature experiments were done in special pressure containers so the water would not change to steam and rupture the apparatus. The samples were placed in gold capsules and sealed to prevent leaks. The investigators made sure that carbon dioxide was also present in the system because it is the main constituent of the Martian atmosphere and must play a role in chemical reactions on the surface. The ratio of carbon dioxide to water varied from 1:3 to 3:1. The experiments ran for seven days.



Schematic diagram for the high temperature experiments. The samples, consisting of basalt powder, were placed in a sealed container with water and carbon dioxide, and heated for seven days.

After each experiment Baker and her colleagues examined the samples by electron microscopy and x-ray diffraction to identify the compounds produced. All the experiments produced an impressive assortment of carbonate minerals, including those containing calcium, iron, magnesium, and manganese. Several forms of pure silica dioxide were produced (opal, cristobalite, and quartz). Hematite (rusty iron oxide) appeared in many of the experiments, as did an array of hideously complicated water-bearing minerals with exotic names such as sacrofanite, vesuvianite, and sepiolite.

Temperature had the most pronounced effect on the nature of the products produced in the experiments. The lowest temperature experiments (23 °C) generally produced only calcium carbonate, magnesium carbonate, and opal or cristobalite. The experiments at 75 °C produced all of those minerals plus iron carbonate, iron and magnesium oxides, quartz, and sacrofanite, one of the complicated

water-bearing minerals. The high-temperature experiments formed these minerals in various combinations, plus an assortment of water-bearing minerals. Exactly which mineral formed depended on the ratio of carbon dioxide to water.

## Martian Meteorites: Intermittent Wetting by a Little Bit of Water

**B**aker and co-workers compared the products of the experiments to the minerals found in ALH 84001 and the nakhlites. The ALH meteorite contains calcium-iron-magnesium carbonates, iron oxides, and traces of silica, but no water-bearing minerals. In contrast, the nakhlites are more extensively altered and contain water-bearing minerals such as clays and hydrated iron oxides. On the basis of the experiments, Baker concludes that the alteration products in ALH 84001 formed at different temperatures than those in the nakhlites.

The experiments suggest that ALH 84001 did not interact with water for a long period. Similarly, long-duration interaction with hot water-poor vapor is also unlikely. Baker and colleagues note that this is consistent with Paul Warren's (University of California, Los Angeles) suggestion that the ALH 84001 parent rock was altered by intermittent soaking of the Martian surface by floods. However, the rapid rate of alteration observed in the experiments also suggests that the wet periods must have been fast, lasting only days rather than weeks or months. Baker also points out that the experiments do not rule out formation of the carbonates and oxides in ALH 84001 by very short exposure to high-temperature gases, as some other scientists have suggested.

Baker and her colleagues also conclude that the nakhlites were not exposed to water for long periods, although they are more altered than ALH 84001. This is consistent with conclusions reached several years ago by James Gooding (Johnson Space Center) and Allan Treiman (Lunar and Planetary Institute). They suggested that the Lafayette meteorite (one of the three nakhlites) was altered by occasional interaction with small amounts of water. So, although altered more than ALH 84001, the nakhlites also did not sit around in either cool or hot water for a long time. Baker hopes that further experiments will be able to allow a more precise estimate of the amount of time and water involved.

#### When?

Tim Swindle and his coworkers from the University of Arizona, the Lunar and Planetary Institute, and the Johnson Space Center wanted to find out when the alteration of one of the nakhlites took place. They analyzed samples from the Lafayette meteorite, which contains the most alteration products of any Martian meteorite. Previous measurements of the age of the meteorite concentrated on the main minerals in the rock, which formed when the rock solidified in magma. Three different isotopic techniques (potassium-argon, rubidium-strontium, and samarium-neodymium) all gave an age of 1.3 billion years. The alteration products must have formed after that time, showing that water was present on the surface in small quantities during the past billion years.



[Tim Swindle, Univ. of Arizona]

Mass spectrometer used by Tim Swindle and colleagues at the University of Arizona to measure the ages of small samples of iddingsite.

Swindle used the potassium-argon technique to determine the age of iddingsite, the rusty mixture of minerals that decorates Lafayette. Allan Treiman carefully picked 25 tiny samples of iddingsite from the meteorite, weighing from 0.5 to 34 micrograms. Then David Lindstrom (Johnson Space Center) measured the amount of potassium in each sample. Finally, Swindle and his colleagues at the University of Arizona measured the argon in the samples, and converted all these measurements into ages. The fact that they could measure the amount of potassium and argon in such minuscule samples is remarkable, but such microanalytical techniques are now commonplace. [See PSRD article Analyzing Next to Nothing.]

Age determinations are almost always tricky, but these were exceptionally so because of the presence of argon from the terrestrial atmosphere, from the Martian atmosphere, and produced by cosmic rays in space. They had to worry about argon loss from the iddingsite--on Mars, in space, during passage through the Earth's atmosphere, and even in the experimental apparatus. Swindle and his colleagues examined all these possibilities in detail, correcting for some, showing that others were insignificant.

The ages of the samples ranged from 0 to about 650 million years. The authors could not determine if the ages represent a range in the formation time of iddingsite or times of alteration of an iddingsite formed earlier. However, because a previously-reported rubidium-strontium age of iddingsite was 679 (plus or minus 66) million years, they suspect that the formation of iddingsite occurred beginning about 650 million years ago and continued for several hundred million years. The old ages also provide further proof that the alteration took place on Mars because the Lafayette meteorite is a very recent arrival on Earth.

#### **Implications for Mars**

Mars experts agree that the wettest period in Martian history occurred early in its history, probably 3 to 4 billion years ago. Nevertheless, these two studies of weathering products in Martian meteorites suggest that small amounts of water were available near the surface of Mars during the past several hundred million years. This might indicate that some process (volcanism, impact) melted permafrost in the upper few hundred meters (or less) of the surface, liberating the water needed to alter the nakhlites. ALH 84001 is much less altered than the nakhlites despite the fact that it is much older. This indicates that it remained dry for almost 4 billion years, suggesting that not all regions on Mars had the intermittent presence of water. Swindle and co-workers suggest that ALH 84001, which probably comes from the ancient highlands of Mars, remained drier because the depth to permafrost in the highlands is much greater than on the lower volcanic plains.

Study of the weathering products in Martian meteorites is just beginning. Further study of the alteration products themselves, additional experiments, and refined age-dating measurements will help us understand the water/climate cycle on Mars. Baker and Swindle are collaborating on a series of experiments to determine how much argon and other noble gases can be incorporated into the alteration products as they form. Even more understanding will come when future missions land on Mars, make careful measurements, and return samples to Earth.

## Additional Resources

Baker, L. L., Agenbroad, D. J., and Wood, S. A., 2000, Experimental hydrothermal alteration of a martian analog basalt: Implications for martian meteorites. *Meteoritics and Planetary Science*, vol. 35, p. 31-38.

Meteorites from Mars from Astromaterials Curation, Johnson Space Center.

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