

**Headline Article**

December 15, 2011



# Formation of Carbonate Minerals in Martian Meteorite ALH 84001 from Cool Water Near the Surface of Mars

--- A new approach to thermometry using isotopic compositions of carbon and oxygen indicates that carbonate minerals in Martian meteorite ALH 84001 formed at  $18 \pm 4$  °C.

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Carbonate minerals in the Allan Hills 84001 meteorite are important because they ought to contain information about the chemistry and temperature of the water they formed in. They are also an important part of testing the idea that the meteorite contains evidence of past life on Mars. Hypotheses for the origin of the carbonates are impressively varied. A key test of the ideas is to determine the temperature at which the carbonates formed. Estimates up to now range from a bit below freezing to 700 °C, too big a range to test anything!

To address the problem Itay Halevy, Woodward Fischer, and John Eiler (Caltech) used an approach that involves "clumped" isotope thermometry, which makes comparisons among different isotopic compositions of extracted CO<sub>2</sub>. This allowed the investigators to use the isotopic abundances of both carbon and oxygen. The results indicate that the carbonates formed at  $18 \pm 4$  °C from a shallow subsurface (upper few meters to tens of meters) pool of water that was gradually evaporating. The wet episode did not last long, leading Halevy and his colleagues to conclude that the environment may have been too transient for life to have emerged here from scratch. On the other hand, if life already existed on the Martian surface this wet near-surface environment would have provided a happy home. An impact blasted the Martian home of ALH 84001, causing a transient heating event, perhaps disturbing the isotopic record...or perhaps not because the event was so short. In any case, the clumped isotope thermometry approach seems to have given a good measurement of the temperature at which the carbonate minerals formed.

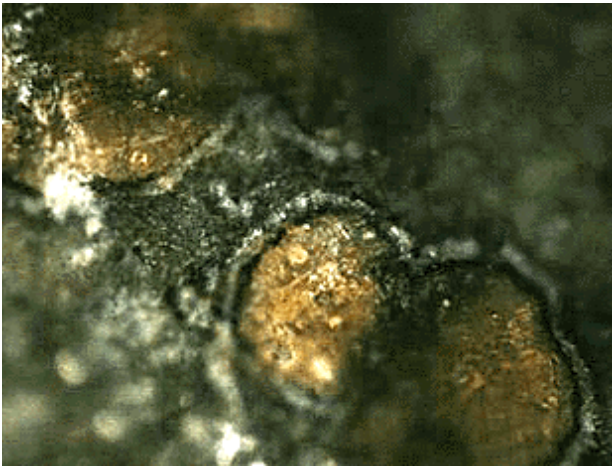
## Reference:

- Halevy, I., Fischer, W. W., and Eiler, J. M. (2011) Carbonates in the Martian Meteorite Allan Hills 84001 Formed at  $18 \pm 4$  °C in a Near-Surface Aqueous Environment. *Proceedings of the National Academy of Sciences*, v. 108, p. 16895-16899. doi:10.1073/pnas.1109444108.
- **PSRDpresents:** Formation of Carbonate Minerals in Martian Meteorite ALH 84001 from Cool Water Near the Surface of Mars --**Short Slide Summary** (with accompanying notes).

## Probing Early Martian Waters

The Martian landscape is decorated with features, such as valley networks, which indicate that surface water flowed in the distant past. The Allan Hills (ALH) 84001 meteorite is an igneous rock that consists of 1–2% carbonate minerals deposited inside the rock. These minerals hold the record of the concentrations of chemicals in the water, the temperature of the water, and possibly the amount of water that flowed through the rock. The meteorite also contains intriguing features that have been interpreted as evidence for past life on Mars (see the 1996 premier article in **PSRD: Life on Mars?**). Carbonates have also been observed from orbit using visible to near infrared spectroscopy, so the occurrence in ALH 84001 carries more general significance for the aqueous geochemistry of early Mars.

In spite of the overt evidence for water having played an important role in shaping the Martian surface before 3.5–3.8 billion years ago, climate models for Mars suggest that it is difficult to produce high enough atmospheric pressure and warm enough temperatures to have abundant liquid water on the surface. The carbonates in ALH 84001 may hold the key to determining how much water flowed on the surface, especially because they formed between 3.9 and 4.0 billion years ago in an igneous rock (represented by most of ALH 84001) that is 4.1 billion years old.



Carbonate globules in the ALH 84001 meteorite contain key information about the temperature at which they formed and the chemistry of the waters in which they precipitated. This NASA image is about half a millimeter across.

Carbonate concretions in ALH 84001 are chemically zoned, with central regions rich in calcium and iron, and rims rich in magnesium. Carbon and oxygen isotopes correlate with composition: Cores have low  $^{18}\text{O}/^{16}\text{O}$  and low  $^{13}\text{C}/^{12}\text{C}$  while the rims have higher values of both isotopic ratios. (Oxygen and carbon isotopic ratios are usually stated as ratios and compared to terrestrial standards, expressed by the notation  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .) Previous research on oxygen and carbon isotopes in the Martian carbonates agree on *neither* the formation temperature, depth of formation, role of impacts, biological activity, or other factors. See, for example, **PSRD** articles presenting conflicting viewpoints:

- **Low-Temperature Origin of Carbonates Consistent with Life in ALH 84001**
- **Shocked Carbonates May Spell N-O L-I-F-E in ALH 84001**
- **Resolution of a Big Argument About Tiny Magnetic Minerals in Martian Meteorite**
- **Did an Impact Make the Mysterious Microscopic Magnetite Crystals in ALH 84001?**

One way to independently determine the temperature of formation is to use clumped isotope thermometry.

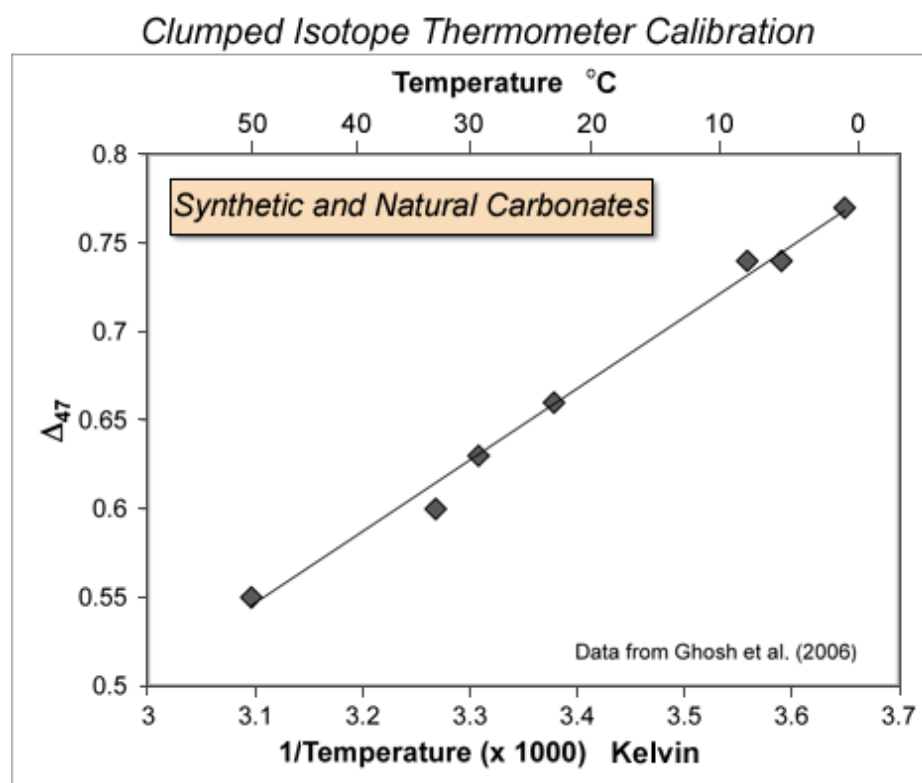
## Clumping Isotopes

Previous estimates of the temperature of formation of carbonates in ALH 84001 required assumptions about the chemistry and isotopic compositions of the water from which the carbonates formed. To get around this problem, Halevy and coworkers focused on measuring the isotopic compositions of "isotopologues" of  $\text{CO}_2$ . Isotopologues have the same chemical composition ( $\text{CO}_2$  in this case), but differ in how much  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$  they contain. There are quite a few combinations, but Halevy focused on  $\text{CO}_2$  with a molecular mass of 47. Mass 47 is particularly useful because it contains both  $^{18}\text{O}$  and  $^{13}\text{C}$ , which show a temperature-dependent preference for sticking together

rather than residing in separate  $\text{CO}_2$  molecules. The advantage of this approach to deriving a temperature of formation is that it is based on thermodynamic equilibrium (chemical balancing) inside the carbonate minerals. Thus, we do not need to make assumptions about the chemical composition of the aqueous fluid to determine the temperature. Even better, once the temperature is known, measurements of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  give direct information about the isotopic composition of the fluids.

The most common isotopologue of  $\text{CO}_2$  has a mass of 44. It is composed of the abundant isotopes  $^{16}\text{O}$  (two of them in each molecule) and  $^{12}\text{C}$ , which accounts for 98% of the abundance of all the isotopologues. After extensive chemical extraction, Halevy measured the abundances of mass 47 and 44 in a mass spectrometer. A particularly informative measurement is the ratio of mass 47 to mass 44, and expressed as  $R^{47}$ . This value is compared to the value calculated from a probability calculation of the R value if the isotopes are randomly distributed among the isotopologues. A final parameter,  $\Delta_{47}$ , is calculated from the R values and reported in parts per thousand.  $\Delta_{47}$  is a measure of the preference of the heavy isotopes for sticking to each other rather than to the lighter isotopes. (You have to know math to do this isotopic stuff, but the chemistry involved in the release of  $\text{CO}_2$  and the instrumentation to measure it are even more daunting!)

Previous work on experimentally produced and natural samples has shown that  $\Delta_{47}$  is correlated with temperature of formation. This empirical correlation agrees well with calculations of the temperature dependence of  $\Delta_{47}$  based on thermodynamic principles. Thus, once  $\Delta_{47}$  is determined, the temperature of formation can be calculated. The actual correlation is between  $\Delta_{47}$  and one divided by the temperature (in Kelvin), a common way to determine how a parameter varies with temperature. The graph below shows a good linear correlation with  $1/T$  and the equivalent temperature in Celsius (shown along the top axis). Once you know  $\Delta_{47}$ , just look up the corresponding temperature in degrees Celsius.



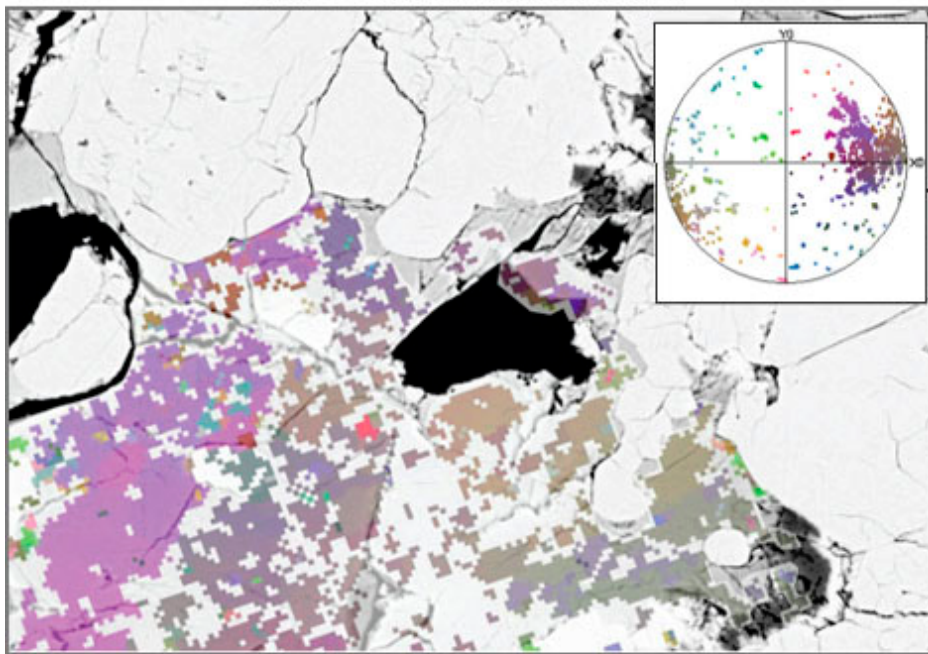
(Data from Ghosh *et al.*, 2006, *Geochimica et Cosmochimica Acta*, v. 70, p. 1439-1456, doi: 10.1016/j.gca.2005.11.014.)

Value of  $\Delta_{47}$  plotted against the inverse of the temperature in Kelvin ( $1/T$ ). The temperature in degrees Celsius is shown along the top. The data form a reasonably straight line, allowing Halevy and coworkers to calculate the temperature at which the carbonates in ALH 84001 formed, once they had determined  $\Delta_{47}$  for the Martian carbonates.

Halevy and coworkers extracted  $\text{CO}_2$  from three samples of ALH 84001, using heated phosphoric acid. For each sample, they did three extractions by treating the samples for 1, 4, and 12 hours. This procedure separates the  $\text{CO}_2$  from the more readily dissolved calcium-rich carbonates from the more resistant magnesian carbonates. One sample turned out to be too small for accurate analyses, but the other two gave six good data points for  $\Delta_{47}$ . The mean temperature calculated from the graph above is  $18 \pm 4$  °C, solidly in the cool temperature range and clearly not like the elevated temperatures some other techniques had given.

Halevy and coworkers explore the uncertainties in the temperature estimate, including whether it represents a single temperature or a range of temperatures. Considering that the rock was shocked by an impact after the carbonates formed, there is a chance that the temperature was disturbed. To search for effects on the carbonate concretions, Halevy used electron-backscattered diffraction to determine the orientations of the carbonate crystal lattice in different areas of a carbonate concretion. The data show that the structure fans out in a systematic way, rather than forming new crystals throughout the concretion as would be expected if the sample had experienced prolonged annealing at elevated temperature.

### Carbonate Concretion in ALH 84001 with Orientation Information



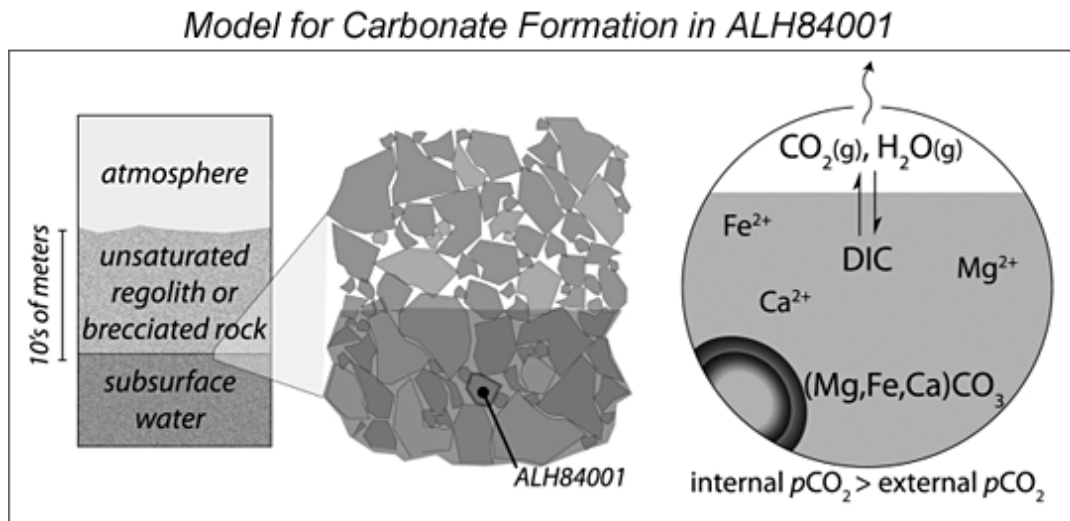
(From Halevy, *et al.*, 2011, *Proceedings of the National Academy of Sciences*, v. 108, p. 16895-16899, doi:10.1073/pnas.1109444108/-/DCSupplemental.)

Electron backscatter image of a carbonate concretion from one of the ALH 84001 samples analyzed by Halevy and co-authors. Colors indicate relative orientation. The small insert shows the direction of the primary crystallographic axis of the carbonate and indicates that it sweeps in a fan-shaped manner, implying radial growth of the crystal. A heating event that caused recrystallization of the carbonates (hence loss of original temperature information) would make the backscatter image and the map of crystal axis orientation blotchy. The lack of recrystallization is consistent with temperature spikes being small and rapid, not enough to significantly alter the record of the original crystallization of the carbonate.

Although the textural evidence for localized, shock heating is strong, the electron backscattered diffraction measurement indicates that these heating events were localized and short. This is supported by the preservation of natural remnant magnetization measurements of the rock (see [PSRD](#) article: [Low-temperature Origin of Carbonates Consistent with Life in ALH84001](#)). Also, studies of argon retention in the rock indicates the rock was not heated significantly after the carbonates formed and the rock remained cold for the past 4 billion years (see [PSRD](#) article: [Martian Meteorites Record Surface Temperatures on Mars](#)).

## Evaporating Fluids, Precipitating Carbonates

Previous measurements by ion microprobe of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in carbonate concretions show that these parameters are correlated with each other and with carbonate major element composition. Combined with the modest, constant temperature determined from the clumped isotope approach, this suggested to Halevy and coworkers that the concretions may have formed by slow evaporation of a shallow subsurface water solution that had soaked cracks and other pore spaces in the rock that would become ALH 84001. The direct correlation between carbon and oxygen isotopic compositions indicates that the water was not in constant, rapid communication with the atmosphere, which would have led to more constant isotopic compositions. Halevy also shows that formation of the carbonates at a range of temperatures, not at constant temperature, is not consistent with the data. It appears that the water evaporated away at the constant temperature of 18 °C, precipitating carbonates and losing carbon dioxide as a gas.



(From Halevy, et al., 2011, *Proceedings of the National Academy of Sciences*, v. 108, p. 16895-16899, doi: 10.1073/pnas.1109444108.)

This diagram illustrates Halevy and co-authors' idea that the carbonates in ALH 84001 were formed when water flowed into the base of a rubbly upper surface of Mars and gradually evaporated. The left diagram shows the physical model, with the rock that would become ALH 84001 sitting in an underground, water-saturated area. The right hand diagram shows the chemical processes taking place: Formation of chemically zoned carbonate concretions from water that contains the appropriate elements in solution along with dissolved inorganic carbon (DIC), and loss of carbon dioxide to the atmosphere above. The water has only a feeble connection to the atmosphere, so both water chemistry and carbonate chemical and isotopic compositions change as the water evaporates.

Similar evaporative deposits occur on Earth in cold or arid regions. Halevy and coworkers cite several examples of studies in which carbon and oxygen isotopes correlate, such as mine tailings in Canada, carbonate deposits in the Houghton impact structure in the Canadian Arctic, carbonates in arid soils in the Mojave and Atacama deserts, and caliche formed on basalts in lava fields in Arizona. The isotopic variations are strikingly similar to those in ALH 84001, but Halevy points out that the terrestrial analogs are far from perfect because of the ubiquitous presence of organic compounds and living microorganisms on Earth. Biology is a key driver of chemical alteration on Earth, so the isotopic trends may be due partly to terrestrial life. Of course, if there was abundant life on Mars...!



Photo of Jay Quade (University of Arizona). Photo credit: Julio L. Betancourt (U.S. Geological Survey).

Jay Quade (University of Arizona) digs a test pit to sample carbonates formed in the arid soil of the Atacama desert, Chile. The region is almost as dry as Mars and has a landscape to match, although microorganisms live in the soil, only 10 inches or so below the surface. Quade and colleague Julio Betancourt (U.S. Geological Survey) and their students are studying the soil carbonates as biomarkers for terrestrial vegetation.



Photo of caliche on basalt from Sunset Crater, AZ. Photo credit: L. Paul Knauth (Arizona State Univ.).

White caliche coats a cavity in a basalt flow in Sunset Crater, Arizona. The caliche may have formed by evaporation, but the green deposit appears to be biological in origin and its formation may have affected the trends produced in  $\delta^{13}\text{C}$ .

The carbonates in ALH 84001, as with other products of water solutions in Martian meteorites and with the aqueous products observed using spectroscopic techniques from orbit, are important for determining the chemistry and abundance of water in early Mars. The record in ALH 84001 seems to point towards a time when temperatures were mild enough that near-surface water was warm, certainly a nice temperature for life, but perhaps scarce or fleeting—conditions less suitable for a healthy lifestyle. We still do not know what made conditions warm. It might have been greenhouse gases in a denser atmosphere, a nearby impact, or nearby volcanic activity. We clearly need samples from many more places to fully understand the early climate history of Mars and its potential for life.

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## Additional Resources

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Links open in a new window.

- **PSRD presents:** Formation of Carbonate Minerals in Martian Meteorite ALH 84001 from Cool Water Near the Surface of Mars --**Short Slide Summary** (with accompanying notes).
- Ghosh, P., Adkins, J., Affek, H., Blata, B., Guo, W., Schauble, E. A., Schrag, D., and Eiler, J. M. (2006)  $^{13}\text{C}$ - $^{18}\text{O}$  bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica et Cosmochimica Acta*, v. 70, p. 1439-1456, doi: 10.1016/j.gca.2005.11.014. [[NASA ADS entry](#)]
- Halevy, I., Fischer, W. W., and Eiler, J. M. (2011) Carbonates in the Martian Meteorite Allan Hills 84001 Formed at  $18 \pm 4$  °C in a Near-Surface Aqueous Environment. *Proceedings of the National Academy of Sciences*, v. 108, p. 16895-16899. doi:10.1073/pnas.1109444108. [[abstract](#)]
- Knauth, L. P., Brilli, M., and Klonowski, S. (2003) Isotope Geochemistry of Caliche Developed on Basalt. *Geochimica et Cosmochimica Acta*, v. 67, p. 185-195, doi: 10.1016/S0016-7037(02)01051-7. [[NASA ADS entry](#)]
- Quade, J., Rech, J. A., Latorre, C., Betancourt, J. L., Gleeson, E., and Kalin, M. T. K. (2007) Soils at the Hyperarid Margin: The Isotopic Composition of Soil Carbonate from the Atacama Desert, Northern Chile. *Geochimica et Cosmochimica Acta*, v. 71, p. 3772-3795, doi: 10.1016/j.gca.2007.02.016. [[NASA ADS entry](#)]
- Scott, E. R. D. (May, 1997) Shocked Carbonates May Spell N-O L-I-F-E in ALH 84001. *Planetary Science Research Discoveries*. <http://www.psrdr.hawaii.edu/May97/ShockedCarb.html>
- 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.psrdr.hawaii.edu/May02/ALH84001magnetite.html>
- Taylor, G. J. (Oct. 1996) Life on Mars? The Evidence and the Debate. *Planetary Science Research Discoveries*. <http://www.psrdr.hawaii.edu/Oct96/LifeonMars.html>
- Taylor, G. J. (May, 1997) Low-temperature Origin of Carbonates Consistent with Life in ALH84001. *Planetary Science Research Discoveries*. <http://www.psrdr.hawaii.edu/May97/LowTempCarb.html>
- Taylor, G. J. (Oct., 2007) Did an Impact Make the Mysterious Microscopic Magnetite Crystals in ALH 84001?. *Planetary Science Research Discoveries*. <http://www.psrdr.hawaii.edu/Oct07/magnetite-origin.html>



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