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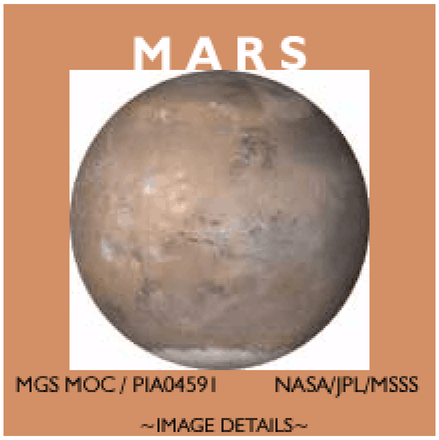

posted October 28, 2003

Show Me the Carbonates

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--- Carbonate minerals intermingle with silicates in the Martian surface dust.

The Martian surface dust is 2 to 5 weight % carbonate minerals. Joshua Bandfield, Timothy Glotch, and Philip Christensen (Arizona State University) reported the result after examining Mars Global Surveyor Thermal Emission Spectrometer (TES) data from 21 high-albedo, dusty surfaces on Mars located between 30°S and 15°N. Trace amounts of carbonates are widely distributed in the silicate-rich dust, but no evidence has been found in the TES data for widespread deposits of exposed carbonate rock. The small amount of detected carbonate is more consistent with the idea that Mars has long been cold and mostly dry rather than a place formerly warm and wet with a thick carbon dioxide atmosphere, and especially favorable for life.

Reference:

Bandfield, J. L., Glotch, T. D., and Christensen, P. R. (2003) Spectroscopic identification of carbonate minerals in the Martian dust. *Science,* v. 301, p. 1084-1087.

Why Look for Carbonates on Mars?

The motivation to search for carbonates on Mars is the mineral's relationship to water. Carbonates form when carbon dioxide gas dissolves in water releasing negatively charged carbonate ions (anions, CO_3^{2-}) that bind to a variety of positively charged ions (cations) such as calcium or magnesium. This means that carbonate minerals precipitate out of carbon dioxide-rich solutions; they form readily in the presence of water and a carbon dioxide atmosphere. If the hypotheses for a ancient thick carbon dioxide atmosphere and water on Mars are true, including an ancient northern ocean, widespread smaller standing bodies of water, and outflow channels (as depicted in the graphic on the right), then one line of evidence would be the presence of carbonate rocks.

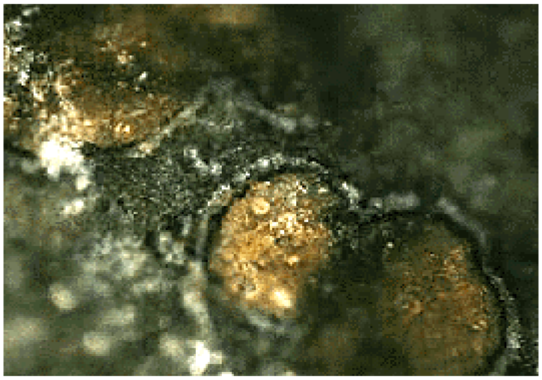
Artist's view of ancient water Chryse Planitia to the Kasei Vallis

Carbonates in Martian Meteorites

Cosmochemical studies of Martian meteorites give us a direct look at water-precipitated minerals including carbonates, salts, sulfates, and clays of extraterrestrial origin (e.g. James Gooding, NASA Johnson Space Center and colleagues). This cosmochemical evidence indicates that water was chemically active on Mars for at least the time span represented by the radiometric ages of the meteorites, that is the past 200-1300 million years. But the Martian meteorites are not severely weathered. The alteration products found in these rocks suggest only intermittent contact with water on Mars [see **PSRD** article "Liquid Water on Mars: The Story from Meteorites."]

Martian carbonate minerals stirred up a commotion in 1996 when a group of scientists from Johnson Space Center, Lockheed Martin, and three universities published a paper in *Science* called "Search for Past Life on Mars: Possible Relic Biogenic Activity in Martian Meteorite ALH84001." ALH 84001 was a slowly-cooled igneous rock in the Martian crust before it was excavated by an impact, altered by fluids, sent to

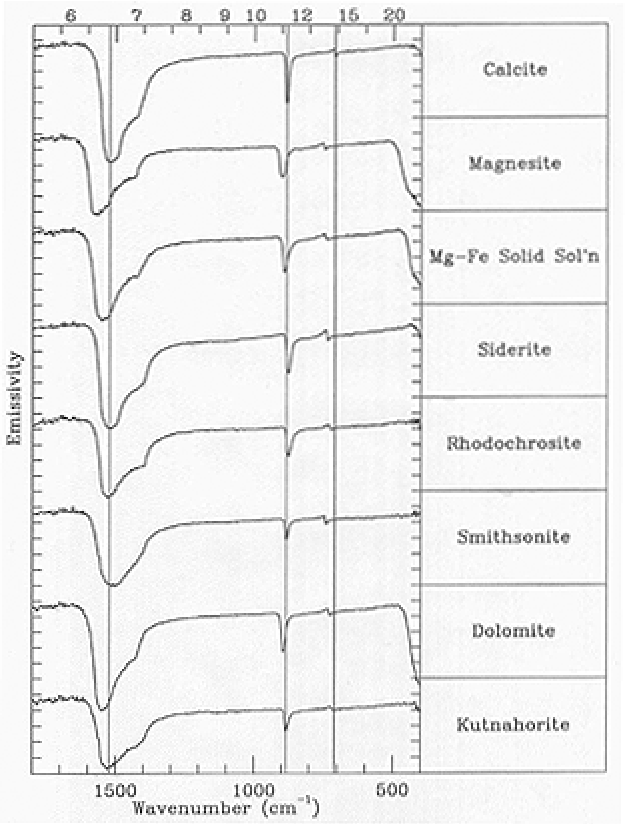
Earth 13,000 years ago by another impact, and finally collected off the Antarctic ice in 1984. The researchers suggested that the meteorite contained evidence of potential fossils within the carbonate globules that were found in crushed zones and cracks in the rock. Fluids rich in carbon dioxide presumably flowed through cracks in the Martian rock depositing globules, plates, and veins of carbonate minerals. Whether these carbonate minerals formed by biologic origin or not and the temperature at which they formed are still issues of debate. [For background, see **PSRD** articles "Shocked Carbonates may Spell N-o L-i-f-e in Martian Meteorite ALH84001," "Low-temperature Origin of Carbonates Consistent with Life in ALH84001," and "Life on Mars?"] Simply and plainly, the existence of carbonates in Martian meteorites confirms the presence of the minerals on Mars.


[NASA]

Finding Carbonates on Mars Remotely

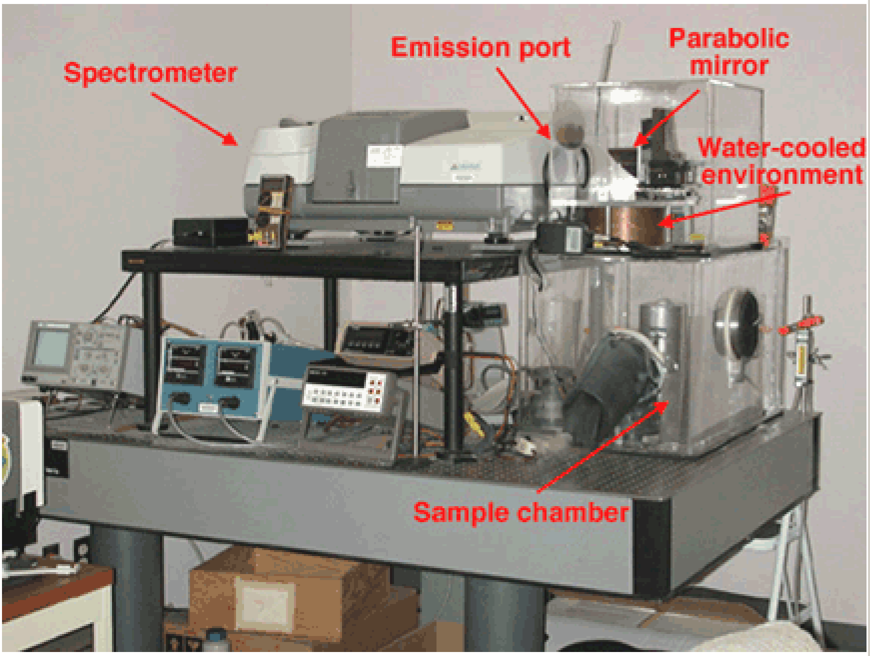
Carbonate minerals have unique absorptions in the near-infrared and thermal infrared spectral regions because of vibrations due to stretching and bending of the carbon-oxygen bonds. Examples of thermal infrared emission spectra of carbonate minerals collected in the laboratory are shown below next to a photo of the instrument used by the researchers.

Thermal infrared emission spectra of carbonates



(Figure from Lane, M.D. and P.R. Christensen (1997) Thermal infrared emission spectroscopy of anhydrous carbonates, *J. Geophys. Res.*, 102, p. 25581-25592.) CLICK FOR LARGER VERSION.

Spectrometer at Arizona State University

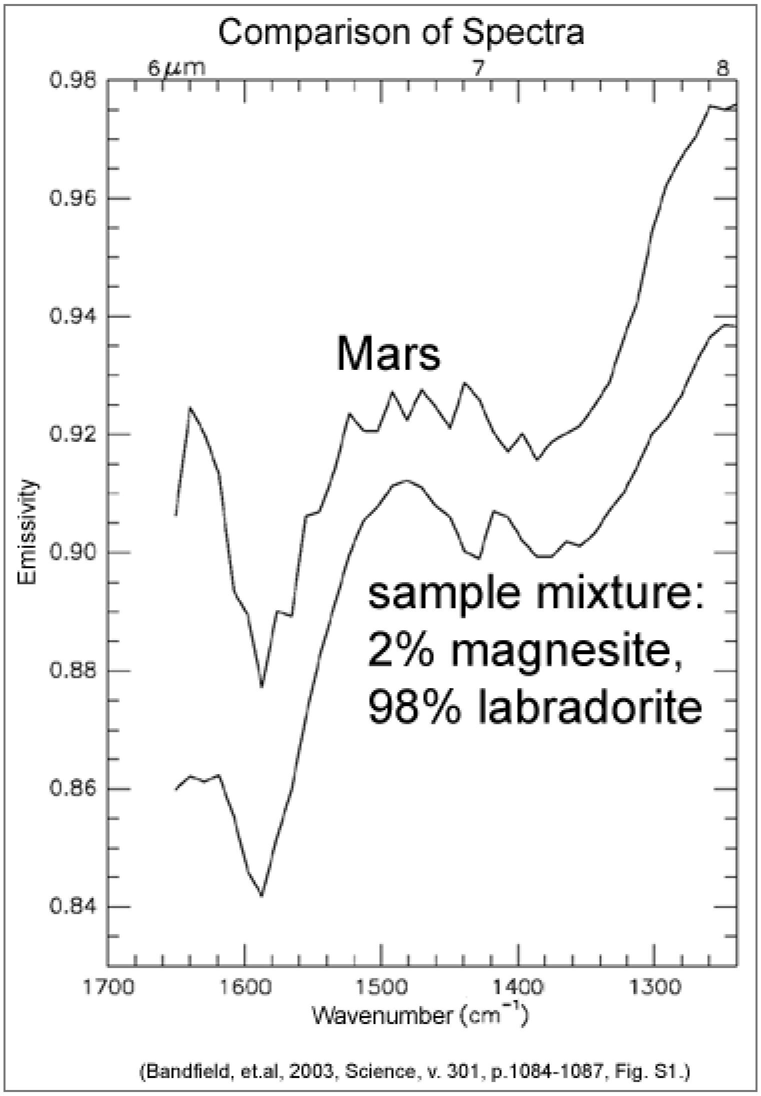


LEFT: Spectra of laboratory samples. The absorption band between 1350 and 1580 cm^{-1} is diagnostic of carbonate minerals. Spectra are offset vertically for easier comparison.
RIGHT: Spectrometer.

Laboratory spectra serve as the standards against which TES data of Mars are compared. Since these comparisons began, no areas of carbonate rocks have been found anywhere on Mars within the resolution limits of the instrument (e.g. areas a few tens of square kilometers.) But this year's new work on the TES spectra by Bandfield and colleagues resulted in the detection of carbonate minerals in the Martian surface dust.

Josh Bandfield and Michael Smith (NASA Goddard Space Flight Center) developed a way to mathematically separate effects of the atmosphere from the surface in the TES data. Their work led to the first detailed spectrum of the dusty surface isolated from the interfering effects of atmospheric dust, water ice aerosols, carbon dioxide, and water vapor.

Then Bandfield, Glotch, and Christensen examined 21 TES sequences from a variety of dusty regions between 30°S and 15°N. Though the 21 sites were in different places there were no detectable variations in the shapes of the spectra, probably because the Martian wind is so effective in mixing and moving the dust over the entire globe.



(Bandfield, et.al, 2003, Science, v. 301, p.1084-1087, Fig. S1.)

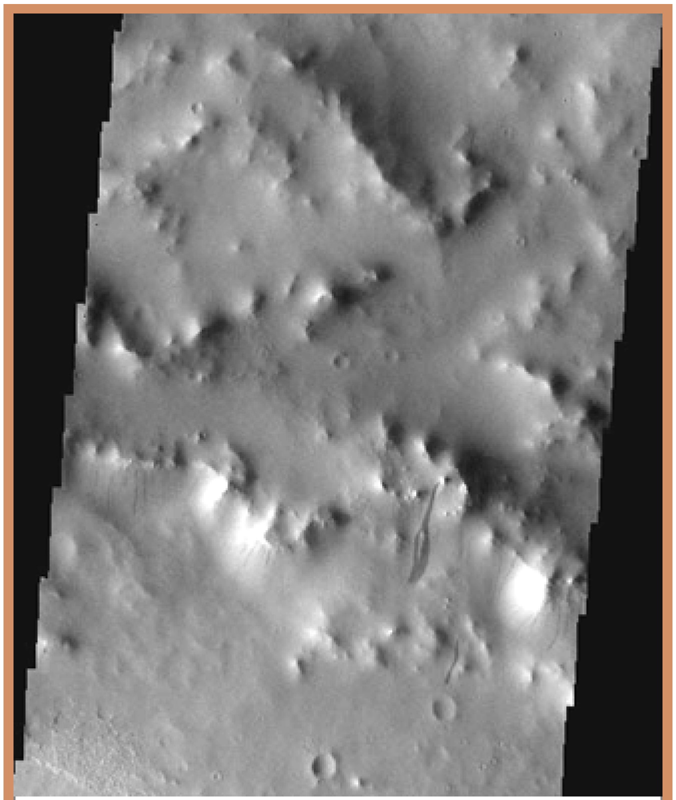
ABOVE: The TES spectrum of the Martian dust (top) matches well with the spectrum of a laboratory sample mixture (bottom) of 98 weight % labradorite silicate and 2 weight % magnesite carbonate ($MgCO_3$) of particle sizes between 0-10 microns. The spectra have been offset vertically for comparison.

The spectrum of the Martian surface dust is shown in the upper curve on the graph shown on the left. To determine the compositions of the materials that can produce such a spectrum, Bandfield and coauthors mixed pure labradorite (calcium sodium aluminum silicate) dust separately with several different carbonate minerals: calcite, dolomite, siderite, and magnesite. Other non-carbonates were also mixed with the labradorite for comparison, including hematite, gypsum, and high silica glass. Bandfield and colleagues chose labradorite as the silicate mineral in their model because of its general similarity to the Martian high-albedo surface spectrum, its purity, and its easy availability. Of all the mineral mixtures tested, only the addition of carbonate minerals and gypsum had any effect on the spectrum of the fine-grained labradorite. Furthermore, the spectral shape between 1350 and 1580 cm^{-1} is unique to materials that contain carbonate minerals, and no other mixture matched the Martian spectrum at these wavelengths. Only the addition of magnesite to the labradorite produced a match with the Martian surface dust spectrum in both magnitude and shape at wavenumbers greater than 1300 cm^{-1}.

The researchers tested the effects of particle sizes of the laboratory samples on the resulting spectrum. They separated labradorite and magnesite into particle size fractions of 0-5, 0-10, 10-20, 20-30, and 30-41 microns. The magnesite dust was added to the labradorite dust in 0.5 weight % increments until the resulting spectrum matched the Martian surface dust spectrum at wavenumbers greater than 1300 cm^{-1}. The 0 to 10 micron particle sizes were the most sensitive to the addition of small amounts of carbonate. They found that the Martian spectrum could be reproduced with at least 2 to 3 weight % magnesite. A tentative upper limit on the abundance of carbonates in the Martian surface dust is set at 5 weight % as suggested by other remote sensing research in the near- and mid-infrared spectral regions. In the final analysis, magnesite may not be a unique answer if future work shows that other carbonate mineral mixtures also match the Martian spectrum. Significantly, these new TES results demonstrate that where there is dust on Mars, there are carbonates in low concentrations.

What a Trace of Carbonates Might Mean

The work by Bandfield and colleagues found that carbonate minerals at concentrations of <5 weight % are common in the Martian surface dust (see the image below for a typical dusty surface). Previous work also recognized carbonates (1 to 3% volume) in the airborne dust using thermal emission spectra of Mars from telescopes (e.g. the Kuiper Airborne Observatory data used by James Pollack and colleagues in 1990). Bits of carbonate minerals have been studied in Martian meteorites. The task is to figure out how these findings of carbonate minerals fit into the history of water and climate on Mars.



THEMIS visible image of Mars (centered near 2°N, 27°W) blanketed by dust that contains several percent carbonates.
~ IMAGE DETAILS ~

Martian dust appears to have ubiquitous low levels of carbonate minerals yet the planet appears to lack carbonate cliffs or outcrops. Does this mean there were no oceans, lakes, or running water on the Red Planet? No, it's not that simple. Carbonates are simply expected as a natural product of weathering in a wet Martian environment, and there are good reasons for thinking that Mars was wet. A variety of surface features are attributed to ancient surface water (e.g. channels, outflow channels) and recent groundwater seepage or snow (gullies) even though water is not stable on the surface of Mars today. Subsurface water ice was detected last year by the Mars Odyssey suite of instruments (see **PSRD** article Dirty Ice on Mars). It is possible that the small amounts of carbonate minerals in the dust are erosional remnants of ancient carbonate source rocks whose formation served as a buffer for atmospheric CO_2. These carbonate rock layers may simply be hidden now beneath layers of the silicate-rich dust. It's also possible that the carbonates were washed underground and are now too deep to be detected by TES.

On the other hand, there are reasons favoring a colder, dryer Mars where extensive carbonate rock layers never formed. It is most probable, say Bandfield and coauthors, that the small amounts of carbonate minerals detected in the surface dust were not derived from carbonate outcrops but formed through the ages by simple reactions between the dust and moisture in the thin Martian atmosphere. Additionally, spectroscopic evidence for clays, which are known indicators of aqueous weathering, remains inconclusive.

The questions of how carbonate minerals formed on Mars and what that means about the environment and climate in which they formed are still being answered. Ultimately, they'll lead us to answers about the duration of surface and near-surface water in Mars' past. In August, 2003 in reference to finding traces of carbonates and what that may mean for water on Mars, Phil Christensen, principal investigator for the TES instrument said, "Maybe instead of calling them oceans, we should call them glaciers. A frozen ocean will not form carbonate. I believe Mars has a lot of water, but it is cold and frozen most of the time. That is consistent with what we have seen."

Additional Resources

Archived news release, August 22, 2003, from Arizona State University.

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Mars Meteorite Compendium-2003

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Thermal Emission Spectrometer (TES) on Mars Global Surveyor (MGS).

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