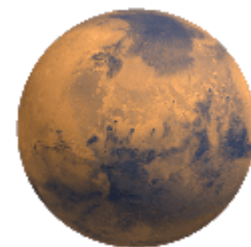


Hot Idea

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Gullies and Canyons, Rocks and Experiments: The Mystery of Water on Mars



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Mars is wet. Or at least it was wet. Vast canyons, numerous gullies, and even possible ocean deposits attest to the presence of abundant water on the planet, but magmas do not seem to have contained much of it. The logical way to transport water to the surface of a planet is in magma that erupts to form volcanoes and lava flows. Where did the water come from if not from magmas? Where did it go? Why are the magmas apparently so dry? Two studies of Martian meteorites may provide answers to these questions. Both use a combination of analyses of meteorites and laboratory experiments. One study, led by Harry Y. (Hap) McSween of the University of Tennessee (UT) and coworkers from UT, the Massachusetts Institute of Technology (MIT), Oakridge National Laboratory, and the University of South Florida, measured the abundances of water-soluble trace elements in crystals in a Martian meteorite. They found the centers of the minerals, which formed first and at high pressure, had much more of these elements than the rims. McSween and coworkers cite data showing that the elements are highly soluble in the presence of very hot water. Experiments at MIT show that magma must have contained about 1.8 wt% H₂O to crystallize the minerals observed in the Martian meteorite studied. The scientists conclude that magmas have delivered lots of water to the Martian surface.

The other study, by Meenakshi (Mini) Wadhwa (Field Museum, Chicago) focused on the concentration of the element europium in six meteorites from Mars. By using experimental data obtained by Gordon McKay and Loan Le (Johnson Space Center), Wadhwa concludes that the magmas in which the meteorites formed experienced varying amounts of interaction with the crust of Mars, which must be oxidized. She suggests that the oxidation is due to chemical reactions of rock and water--probably the same water that carved the surface features on Mars.

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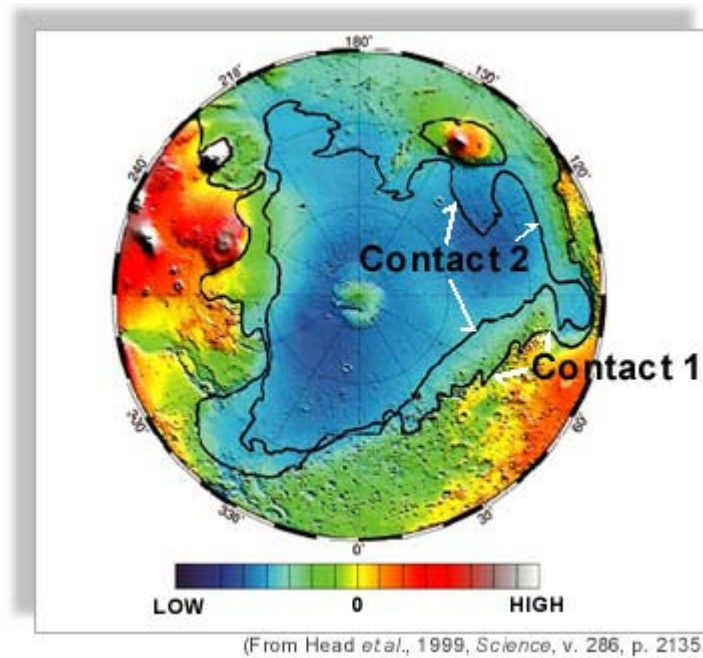
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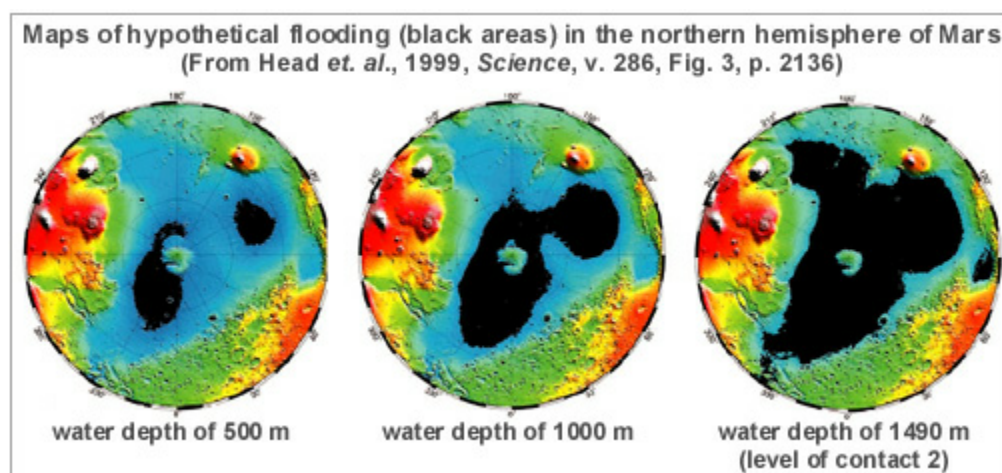
A Surface Carved by Water

Mars orbiter missions have returned a dazzling array of pictures and other information about the Martian surface. We knew from the old Viking images that vast canyons and dendritic river systems dissected the planet's surface. There were hints of dried lake beds [see [PSRD article: For a Cup of Water on Mars](#)] and even a large northern ocean.

High-resolution images from Mars Global Surveyor bolster those old interpretations. Using topographic data obtained by a laser altimeter (MOLA) onboard the spacecraft, James Head (Brown University) and coworkers showed that a large part of the northern hemisphere is a basin with a smooth floor. Although bone dry now, this region might once have been a Martian sea.

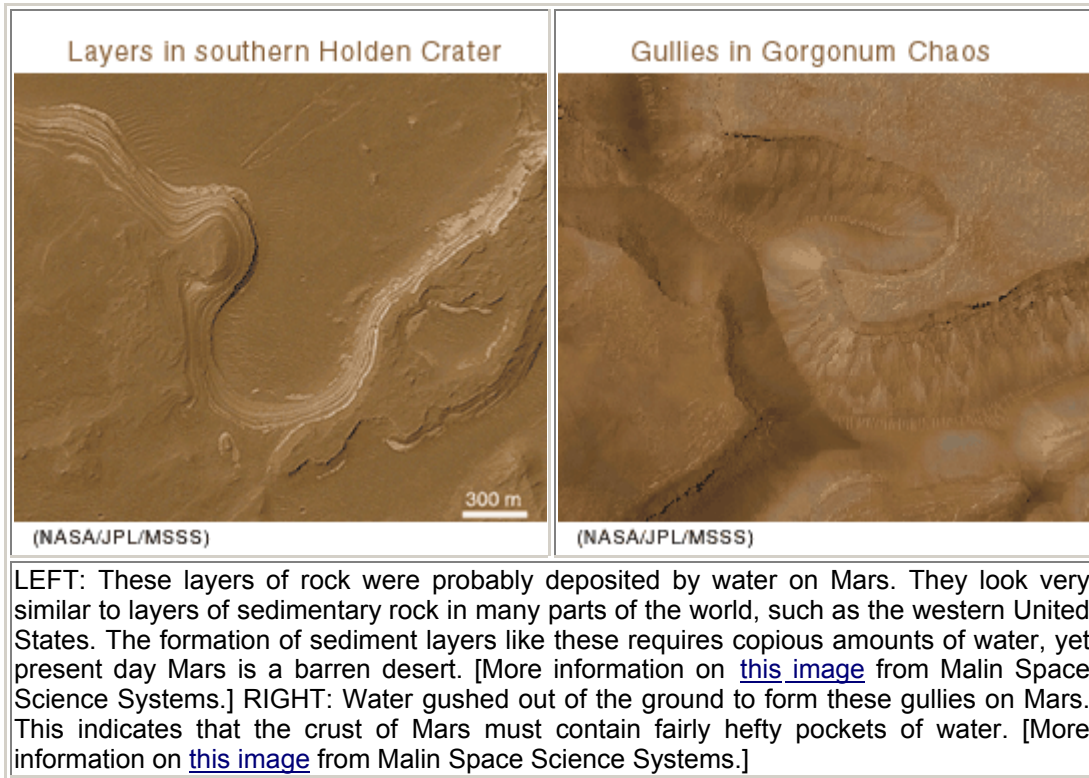


In the late 1980s, researchers looking at Viking images speculated that large bodies of water once filled the low, flat plains of the northern hemisphere on Mars. They cited distinctive landforms indicative of water-related erosional or depositional processes. Timothy Parker and colleagues at the Jet Propulsion Lab mapped boundary contacts between landforms in the northern lowland plains. In their 1989 paper published in *Icarus*, they outlined two contacts that are generally parallel to the southern boundary of the northern lowlands, and interpreted them as representing two separate highstands of a now vanished ocean. The color-coded map shown above is centered on the north pole and shows MOLA data of the topography of the northern hemisphere of Mars. Low elevations are shown in shades of blue. Black lines indicate positions of possible ancient shorelines labeled contact 1 and contact 2.



Using the MOLA topographic data and computer modeling techniques, Head and his colleagues created maps to show the northern lowlands after flooding. They observed where water would pond and how oceans might evolve with changing water depths. The three maps show MOLA elevation data, with black areas representing flooded regions. The map on the far left shows that a water depth of 500 meters would flood two distinct basins in the northern lowlands. At a water depth of 1000 meters, middle map, the basins connect. If enough water were poured back on Mars (a depth of 1490 meters), it would fill up right along the proposed contact 2, as shown in the third map.

Other Mars Global Surveyor pictures show rock layers that look like layers of water-deposited sedimentary rocks on Earth. This indicates extensive regions covered with water at some time in the deep Martian past. Other images show young gullies that probably formed when water gushed from canyon walls relatively recently.



It appears that Mars was once drastically different from the desert it is today. Where is all that water now? If it is in the crust, as water or bound to minerals such as clays or salts, the crust would be oxidizing. Mini Wadhwa shows that, sure enough, the crust is much more oxidizing than the mantle.

Two Rare Elements

Most of us do not spend a lot of time thinking about the elements europium and gadolinium. Geochemists ponder them often because these rare elements (and a bunch of others) are incredibly informative about how a planet's crust forms, interacts with the atmosphere and hydrosphere, and whether it is recycled into the underlying mantle. It's a case of better understanding through chemistry.

Europium (Eu) and gadolinium (Gd) are both rare earth elements. They behave in predictable ways during geological processing. Europium has the added virtue of occurring in two different oxidation states, as doubly-charged (Eu²⁺) and triply-charged (Eu³⁺). Gadolinium is less chemically moody and remains as triply-charged Gd³⁺. The lucky thing is that Gd behaves almost exactly like Eu³⁺, so geochemists can figure out the amount of Eu in each valence state from the total amount of Eu and the amount of Gd. This is a big deal because the ratio of doubly to triply charged Eu is proportional to the amount of available oxygen--the oxidation state--of the environment in which a rock forms. So in principle, if you can figure out the ratio of doubly to triply charged europium, you can determine the oxidation conditions. Gordon McKay and his colleagues at the Johnson Space Center have spent years calibrating the relation between oxidation conditions and europium charge. They actually assess the way the ratio of europium to gadolinium changes with oxygen availability, assuming gadolinium behaves exactly like triply-charged europium. The oxidation conditions are expressed in terms of the oxygen fugacity, a measure of the availability of oxygen to react. This strange-sounding property is measured in tiny fractions of Earth's atmospheric pressure. Typical values are in the range of one billionth to one trillionth of an atmosphere.

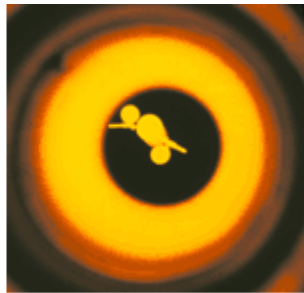
Because the numbers are so tiny, they are usually expressed as a logarithm and often compared to some kind of standard conditions such as the free oxygen associated with an assemblage of the minerals quartz (SiO_2), fayalite (Fe_2SiO_4), and magnetite (Fe_3O_4), or iron metal and iron oxide (FeO). Besides making the comparisons easier, it gives the experimentalists the opportunity to use sentences like, "The oxygen fugacity is plotted in log units relative to the IW buffer." IW refers to iron metal and wustite, another name for FeO . Use it a few times and you begin to think you know what it means. If there is more oxygen than present with iron and FeO , there will be no metallic iron present. You would get the quartz-fayalite-magnetite combination at an oxygen pressure over a thousand times higher (three log units) than when only iron metal and FeO are present.



(Gordon McKay, Johnson Space Center)

To determine how the ratio of europium to gadolinium varies with oxygen pressure, McKay and his coworkers use a high-temperature gas-mixing furnace. They hang a glassy experimental bead from a platinum wire loop, and place it in the hot part of a tube-shaped furnace. A thermocouple monitors the temperature to ensure it remains constant. Available oxygen (the oxygen fugacity) is controlled by passing a mixture of gases through the furnace. Typical mixtures use combinations of carbon dioxide, carbon monoxide, and hydrogen.

Ms. Loan Le suspends an experimental sample in a furnace at the Johnson Space Center.



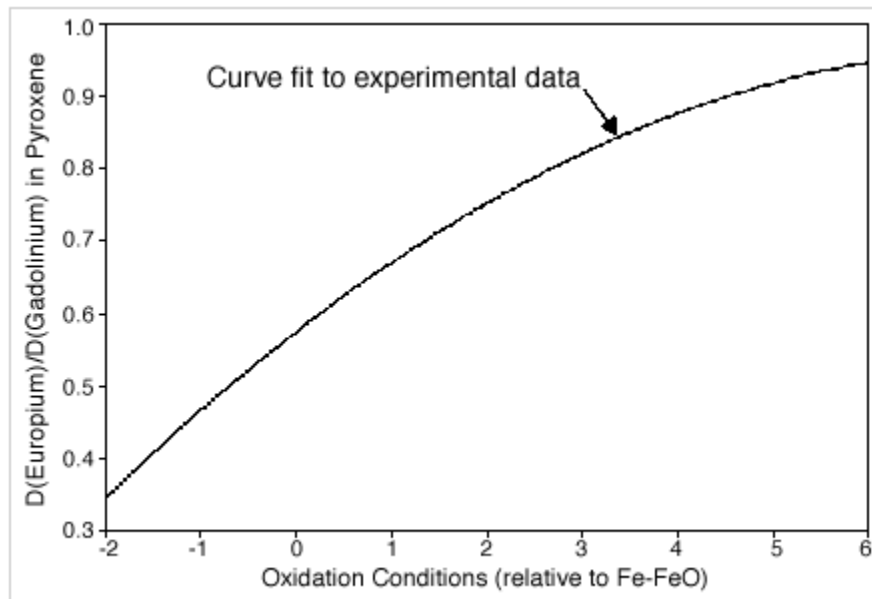
LEFT: A close-up view of two experimental charges on platinum loops hanging from a white ceramic rod. The rod contains the thermocouple wires used to monitor the temperature inside the furnace.

RIGHT: This is what you see if you look down a hot tube furnace: the thermocouple wires and round charges glowing in the hot furnace. The temperature is about 1100 °C.

(Gordon McKay, Johnson Space Center)

The experimental charges are heated for a few days at a temperature low enough for minerals to crystallize from the molten beads. After heating, the charges are dropped from the furnace, cut up and polished, and the abundance of europium and gadolinium in the minerals is measured with an electron microprobe. McKay, Le, and their coworkers have completed a large set of experiments on charges with compositions similar to the magmas they wish to study and close enough to those of Martian meteorites to be useful. A few experiments with compositions identical to Martian meteorites confirmed that the experiments are relevant.

They found that the ratio of europium to gadolinium in the mineral [pyroxene](#) (which is abundant in Martian meteorites) increases with increasing oxidation. This is important because knowing this ratio in a Martian meteorite allowed Mini Wadhwa to determine the oxidation state of Martian magma.



(PSRD graphic based on data from Gordon McKay.)

Variation of the europium to gadolinium ratio versus oxidation conditions (expressed as deviation from conditions when both iron metal and iron oxide are present). The element ratio in the mineral pyroxene has been divided by the same ratio in the starting composition. This procedure gets rid of the effect of different starting concentrations of the elements. The more oxidizing the conditions (to the right on the x-axis), the higher the ratio of europium to gadolinium. If you know this ratio in a pyroxene crystal in a rock, you can determine the oxidation conditions under which the rock formed.

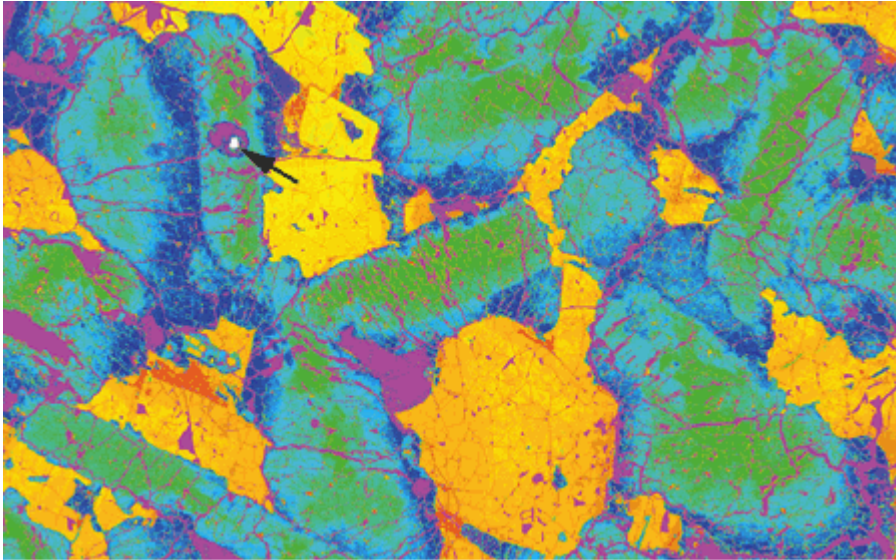
The Oxidation State of the Martian Crust

Mini Wadhwa is an expert on Martian meteorites. She is especially skilled in measuring the concentrations of elements present in tiny amounts, using a complicated tool called the ion microprobe. This device works by focusing a high-energy beam of ions (usually oxygen, argon, or cesium) onto a polished sample. The beam digs a hole while sputtering all the elements in the sample into a cloud of neutral atoms and ions. The ions are accelerated into a mass spectrometer, where they are magnetically separated by mass and then counted. The concentrations of elements in the sample are calculated by comparison with minerals of known composition. There are some tricky corrections to be made, but analysts have figured out how to make them.



Ion microprobe at Washington University in St. Louis, which Mini Wadhwa used to measure the concentrations of europium and gadolinium in Martian meteorites.

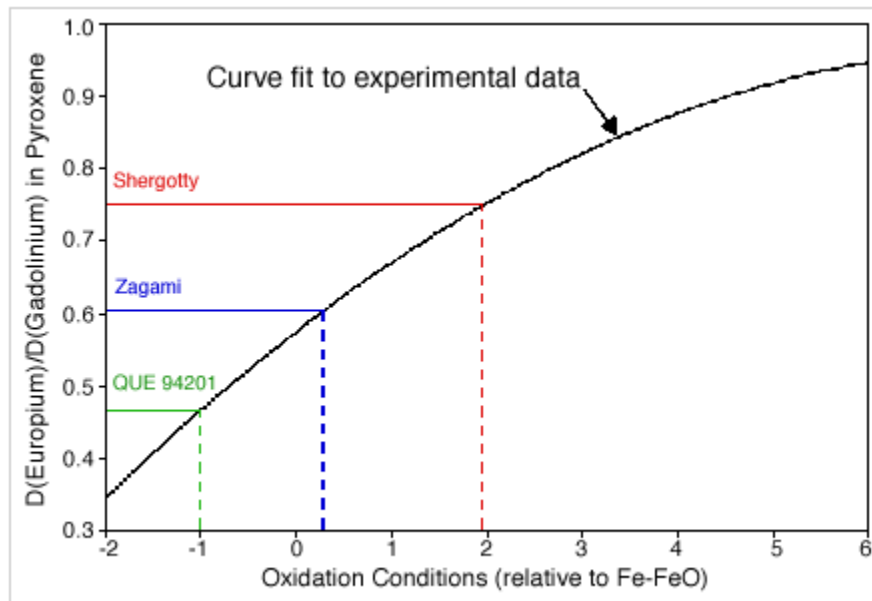
Wadhwa concentrated on a group of Martian meteorites known as the [shergottites](#). (The group was named after its first member, the Shergotty meteorite, which fell in India in 1865.) These originated as lava flows on Mars, and have not been modified much since they erupted, except for some slight weathering while on Mars and the trauma of being blasted off the planet. Wadhwa's goal was to measure the europium/gadolinium ratio in the pyroxene crystals inside the Shergottites, then use McKay's data to determine the oxidation state.



(Meenakshi Wadhwa, Field Museum)

Colorized image of a polished slice of the Shergotty meteorite taken with a scanning electron microscope. Blues and greens show the pyroxene grains; yellow corresponds to plagioclase feldspar. Notice that the pyroxene grains are greenish in the interiors and bluish closer to the edges. This indicates that they are chemically zoned, which Hap McSween and his coworkers used to understand changes as the magma rose to the surface of Mars. The white spot indicated with a black arrow is an ion-beam hole (about 30 micrometers in diameter) on one of the areas Mini Wadhwa analyzed as part of her study.

Wadhwa studied seven shergottites. Their Eu/Gd ratios in pyroxene divided by that in the bulk rock sample ranged from 0.75 in Shergotty to 0.44 in Antarctic meteorite QUE 94201. These correspond to a large range in oxidation conditions, from about 100 times the iron metal-iron oxide level to about 0.1 that level.



(PSRD graphic based on data from Gordon McKay and Meenakshi Wadhwa.)

Eu/Gd ratios in pyroxene allowed Mini Wadhwa to determine the oxidation conditions experienced by the magmas from which each meteorite formed. To use the diagram you read the measured Eu/Gd and read across the diagram until that amount intersects the experimental curve determined by Gordon McKay and his colleagues. A line drawn straight down shows the deviation of the oxygen fugacity from that prevailing when the fugacity is controlled by the presence of iron metal and iron oxide.

Wadhwa figured out the oxidation state of the shergottite magmas, but she wondered whether it reflected different oxidation states in the mantle (where the magmas originated) or in the crust (which the magmas had to pass through). To answer this question, she used published analyses of the isotopic compositions of neodymium and strontium. The isotopes of these elements are used to determine rock ages, but they are equally useful in tracking geochemical processes. In this case, Wadhwa used the isotope ratios to assess the amount of contamination by the Martian crust experienced by the magma in which the shergottites formed. This is possible because a planet's crust has a different ratio of, for example, strontium-87 to strontium-86 than do the deeper rock layers in the mantle.

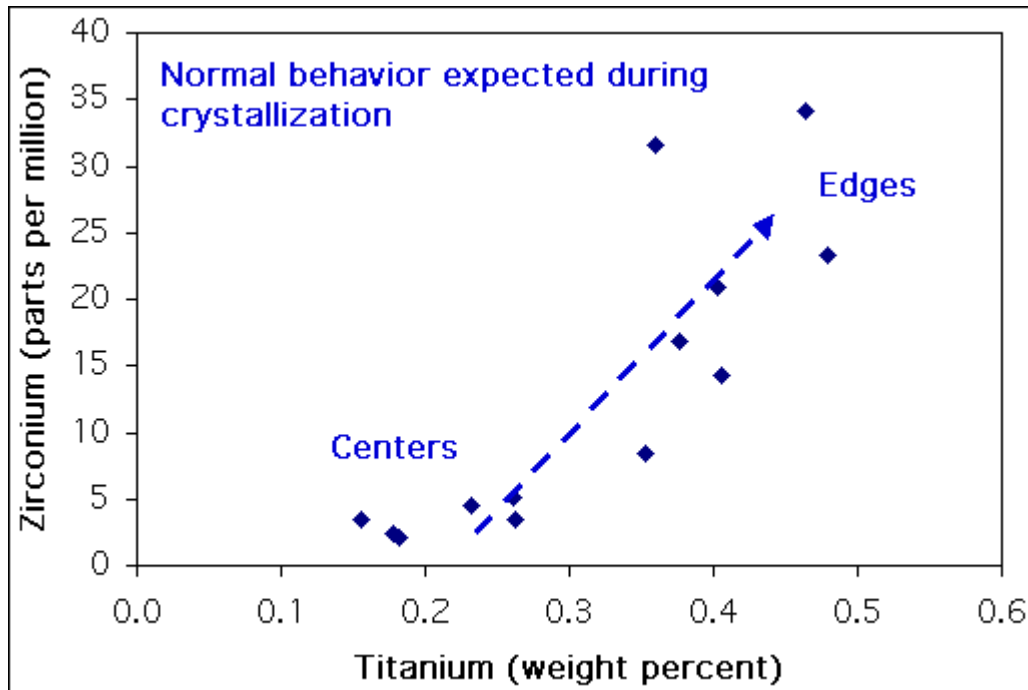
Wadhwa found that the more oxidized a sample is, the higher its strontium-87/strontium-86 ratio. For example, the least oxidized sample, QUE 94201 (see diagram above), has a ratio of 0.701. In contrast, the most oxidized sample, Shergotty, has a strontium-87/strontium-86 ratio of 0.723. The other samples are in between. This suggests that Martian magmas are not very oxidized when they are made by melting in the mantle, but that they become more oxidized as they pass through the crust before erupting. Some become much more oxidized than others. Wadhwa suggests that the crust is oxidized by water circulating in the crust, forming water-bearing minerals. This circulating water may have flowed on the surface in the distant past to carve the valleys and canyons that decorate the Martian surface. How is the water transported to the surface? The work of Hap McSween and his coworkers suggests that Martian magma contained plenty of water that bubbled out as it neared the surface.

Wet Magma

The logical way to transport water to the surface of a planet is in magma that erupts to form volcanoes and lava flows. Near the surface any water dissolved in the magma escapes into the atmosphere because a decrease in pressure lowers the [solubility](#) of the water. An analogy is a can of soda which makes bubbles of carbon dioxide when pressure is reduced by popping the top. The problem with the Martian volcanic meteorites is that they contain very little water. However, Hap McSween and his coworkers show that at least one Martian meteorite, Shergotty, did contain lots of dissolved water. It lost it as its magma approached the surface. [[Cartoon](#) of loss of water in Shergotty.]

McSween has two lines of evidence. First, his colleagues measured the abundances of trace elements such as titanium, zirconium, cerium, lithium, and boron in pyroxene mineral grains. As shown in the colorful image of Shergotty above, the pyroxenes are chemically zoned. This happens because the minerals begin to crystallize at depth (where the pressure is high) and continue to crystallize as the magma ascends (at progressively lower pressure). They measured the abundances of the trace elements with an ion microprobe at Oakridge National Laboratory.

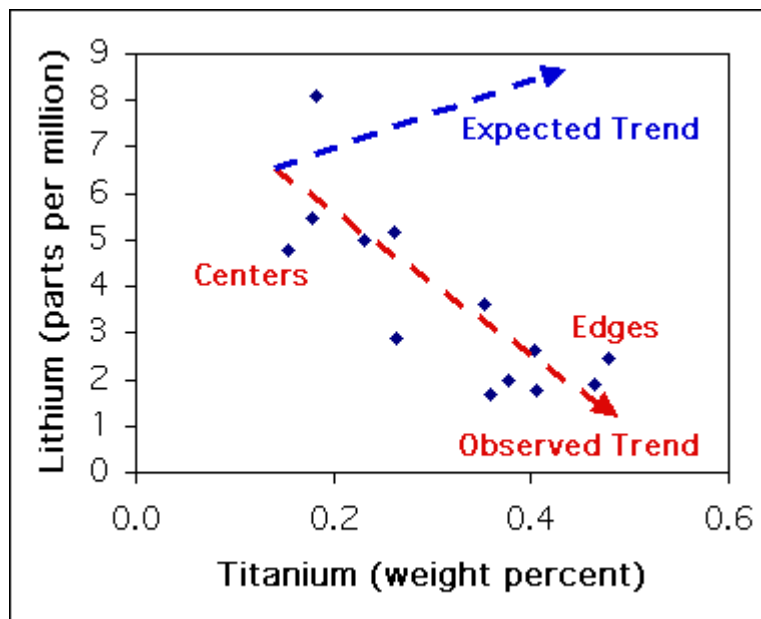
The set of elements they measured normally behave in a very predictable manner. None is incorporated readily into growing pyroxene grains, so as pyroxene crystallizes, the remaining magma ought to become enriched in those elements. This is the case for some of them, such as zirconium and titanium, as shown below.



(PSRD graphic based on data provided by Rachel Lentz.)

As a magma crystallizes pyroxene, both titanium and zirconium increase in the remaining magma. This causes the edges of pyroxene crystals to have higher concentrations of both elements.

This normal behavior is not shown by boron, lithium, and cerium. Instead of increasing as crystallization proceeded, they decreased. McSween and his colleagues figured out that this seemingly perverse behavior is probably caused by the loss of substantial amounts of water from the magma. Experiments show that lithium and boron (and probably cerium, too) are quite soluble in hot water, implying that as water steamed from the magma as it neared the surface, the soluble elements followed the bubbling water. This explains why those elements are much lower in abundance on the outer portions of the pyroxene grains.



(PSRD graphic based on data provided by Rachel Lentz.)

Lithium (and also boron and cerium) decrease as pyroxene grains crystallized in Shergotty, rather than increasing as expected. This seemingly deviant behavior may have been caused by the loss of water from the magma because lithium and the other elements are quite soluble in hot water.

How much water was present in the Shergotty magma? To answer that question, Tim Grove, Jesse Dann, and Astrid Holzheid (MIT) did some experiments to figure out the conditions of formation of the two types of pyroxenes in the rock. They determined the nature of the pyroxenes formed under water-free and water-bearing conditions. Using their data and previously published experiments, they infer that the Shergotty magma contained 1.8 wt% H₂O before it began to lose water. They suggest that the water was still dissolved at a depth of about 5 kilometers.

McSween and colleagues suggest that the water in the Shergotty magma came from either the Martian mantle or was scavenged from a wet Martian crust, as Mini Wadhwa argues. Whatever the ultimate source for the water, McSween and his coworkers conclude that a substantial amount of water was delivered to the Martian surface by volcanic eruptions.

Water on Mars: An Interdisciplinary Problem

Deciphering the history of water on Mars is essential for understanding the geologic evolution of the surface, the extent to which the crust is recycled back into the mantle, and the chances that life originated on the planet. As befitting such an important problem, many types of studies are needed, including analyses of photographs, remote sensing data, in situ analyses by rovers, detailed analyses of samples, and a battery of supporting experimental and theoretical studies. McSween's and Wadhwa's studies use high-tech analyses of meteorites combined with experimental data to understand how water is delivered to the surface of Mars and how water might be distributed throughout the crust.

Additional Resources

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[Missions to Mars](#) from Solar System Exploration, NASA Office of Space Science.

[MOC Images Suggest Recent Sources of Liquid Water on Mars.](#)

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