Self-Reversing Minerals Make a Comeback

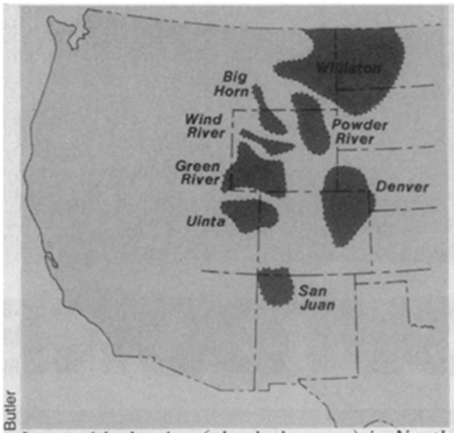
By STEFI WEISBURD

Two and a half decades ago, a rather obscure mineral called titanohematite captured the geologic limelight because of its odd ability to become magnetized in a direction opposite to that of the earth's magnetic field. This neat trick caused all sorts of trouble for geoscientists, who were at the time debating the seemingly unlikely notion that the earth's magnetic field periodically reversed direction. When the dust finally settled, however, the concept of the earth's field reversals was firmly entrenched in geologic thinking, and titanohematite and other so-called self-reversing minerals were shown to be quite rare and were practically forgotten.

Now the pendulum of attention may be swinging back toward these strange minerals. Titanohematite has recently been found to be the dominant magnetic mineral at three sites — a lava field and two sedimentary basins — indicating to the scientists who found it that it may not be as rare as people think. These findings in no way challenge the field-reversal theory, but they could complicate the analysis of the magnetic orientations of rocks that help scientists date lava beds. And because self-reversing titanohematites form under a particular set of conditions, it is also conceivable that their presence could help volcanologists understand the magma (molten rock that flows up through a volcano) systems of volcanos they study.

Rocks become imprinted with a magnetic field when the magnetic moments (intrinsic magnetic fields) of their atoms line up in the direction of the applied field. In volcanic rocks, this atomic geometry is frozen in place as the lava cools. This means that lava flows act as a record of the earth's magnetic field as it existed in the past — provided, of course, that all the minerals record the field in the same way.

A self-reversing mineral, however, would change the rules of the game. It is easy to see, then, how the discovery in 1951 of self-reversing minerals in the dacite (silca-rich volcanic rocks) lava fields of Mt. Haruna in Japan led many geophysicists to doubt the field-reversal hypothesis and to conclude instead that the findings of rocks magnetized differently than the earth's field were due to the antics of some peculiar minerals. But subsequent research, using newly improved dating techniques, proved otherwise. The field-reversal idea triumphed (which is fortu-



Butler

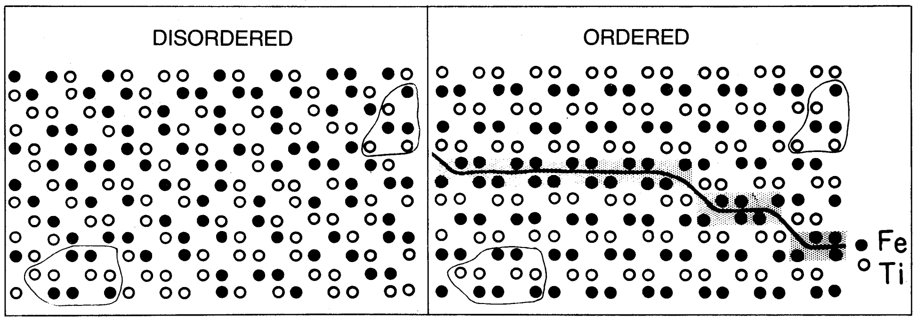
Laramide basins (shaded areas) in North America. Titanohematites cropped up unexpectedly in the continental deposits of the San Juan and Big Horn basins. They have also been found in the Williston Basin, although their extent there is not yet known.

The secret of self-reversal

The self-reversing magic performed by titanohematites has captivated many researchers over the last 30 years in spite of the mineral's relative rarity in nature. By the late 1950s, scientists who had pondered and probed both naturally occurring and laboratory-made samples had a general idea of how self-reversals work.

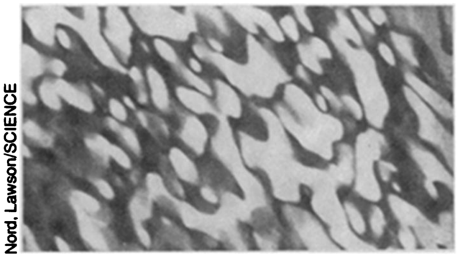
The mineral's trick, they concluded, must be to form two kinds of regions, differing in composition and structure, as it cools from a high temperature in the earth's magnetic field. One region, dubbed the X-phase by the Japanese researchers who first identified it, would have a higher Curie temperature (the temperature below which the mineral becomes magnetized) than the other region. So, as the mineral cools, the X-phase is first to acquire a magnetic field and this field is parallel to that of the earth. At lower temperatures the second region, too, becomes magnetized. But as a result of some interaction between the two types of areas, the second region takes on a magnetic field in the opposite direction to that of the X-phase, and hence to that of the earth.

"The Japanese noticed that there was something that had a higher Curie temperature than the bulk material," says Ken Hoffman in the physics department



Lawson/March 1984 GRL

Formation of antiphase domains (APDs) in a titanohematite mineral. The figure at left shows a nearly random, disordered distribution of titanium and iron cations in the crystal. As the cations move from site to site at high temperatures, small regions of ordered distributions (shown inside the two loops) begin to form, containing alternating rows of titanium and iron cations. At right, these ordered regions have grown (beyond the loops) and become locked in place as the sample cools. Here two ordered regions are shown, but the pattern of iron and titanium rows is mismatched, or out of phase, between the two—hence the term antiphase domains. The boundary between the two ordered regions is called the APD boundary and is thought to contain mostly iron with a disordered sprinkling of titanium. Its size depends on the thermal history of the sample.



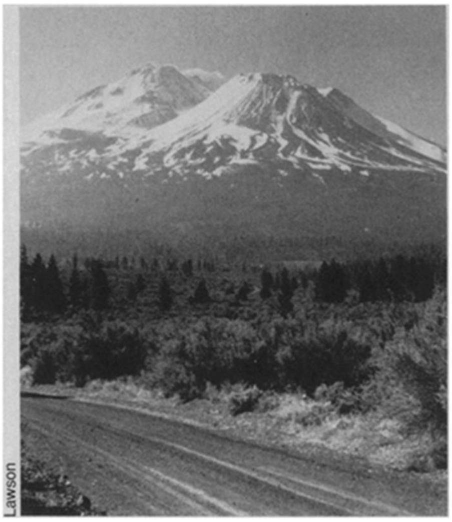
Nord, Lawson/SCIENCE

Transmission electron microscope image (magnified 100,000 times) of a synthesized titanohematite sample clearly shows that this self-reversing mineral formed two kinds of regions as it cooled. The light areas are highly ordered antiphase domains and the dark surrounding areas are less ordered boundary regions.

nate because it went on to provide the last, critical piece of evidence in support of seafloor spreading and plate tectonics), and magnetite, a mineral that records the earth's field with great fidelity, was shown to be the dominant magnetic carrier in rocks. Titanohematites and other self-reversers, it was concluded, are an oddity, excruciatingly rare.

Exactly how uncommon self-reversers are, however, may again be open to question. In 1981 and 1982 self-reversing titanohematites were discovered in Alaska and Canada. And two years ago, Duane E. Champion and Robert L. Christiansen of the U.S. Geological Survey in Menlo Park, Calif., found a wealth of titanohematites in lava flows of California's Mt. Shasta, dating back about 10,000 years. "We have a rather extended episode of time, at least 1,000, perhaps as much as 2,500 years of multiple eruptions that produced this mineralogy," says Champion. "That's unexpected and kind of crazy."

On the basis of Mt. Shasta and the other lava fields in which titanohematites were found, Champion suspects that the mineral is often associated with explosive eruptions. This suspicion is supported by laboratory experiments in which synthetic self-reversing titanohematites were made by rapidly cooling, or quenching, a heated mixture (see sidebar). In an explosive eruption, the shower of hot lava that streams out of the volcano would be quickly cooled too. Champion and others point out, however, that many explosive volcanos have churned out magnetite and not titanohematite, so other factors are probably involved.



Mt. Shasta

One other known constraint on the formation of titanohematites is oxygen. Molten lavas that contain the elements oxygen (O), iron (Fe) and titanium (Ti) can crystallize upon cooling into either the magnetite (Fe_3O_4)-ulvöspinel (Fe_2TiO_4) family or the ilmenite ($FeTio_3$)-hematite (Fe_2O_3) series, to which titanohematites belong. Highly oxidizing environments will produce the latter, whereas reducing magmas favor the former.

Champion believes that the presence of titanohematites, as well as the way in which the lava bed formed, indicates that the magmas erupting at Mt. Shasta 10,000 years ago were highly oxidized *before* they reached the surface. His reasoning is based in part on the fact that gas-charged magmas would also be highly explosive. Champion has found that the quickly cooled pumiceous ash deposits contain essentially one kind of self-reversing titanohematite, whereas lava that cooled slowly in the domes at the surface contains a potpourri of differently composed titanohematites. And of these dome minerals, many are more normally polarized than their pumiceous counterparts. To Champion, this all indicates that the already-formed titanohematites were altered at the surface, not created there.

While he has not seen Champion's data, Ian S. Carmichael, an igneous petrologist at the University of California at Berkeley, disagrees with his analysis. Instead, Carmichael suspects that all the titanohematites resulted from the magma interacting with the oxidizing atmosphere of the earth. The presence of titanohematites at the surface does not reflect an intrinsic

at California Polytechnic State University in San Luis Obispo. "But they couldn't really see it magnetically. ... They could only tell indirect effects of it on the bulk material."

Recent electron microscopy of self-reversing titanohematite samples by Charles Lawson and Gordon Nord Jr. at the U.S. Geological Survey in Reston, Va., confirmed experimentally that two regions are indeed involved. Hoffman, Lawson and Nord believe that the islands of lighter material shown in the photograph at left are so-called antiphase domains (APDs) consisting of a highly ordered material laced with alternating planes of titanium (Ti) and iron (Fe) cations. Surrounding these islands is the APD boundary region (corresponding to the Japanese's X-phase), which the researchers think is rich in iron and relatively disordered in its titanium cation arrangement. With less titanium, the boundary region has a higher Curie temperature than the APDs and so becomes magnetized first.

Hoffman believes that the honeycomblike network of APD boundaries gives them a magnetic rigidity that keeps the magnetic moments of the cations within locked in the direction of the earth's field when the APDs become magnetized. The final magnetic polarity of the rock's magnetic field is reversed, the researchers say, because the APDs are so much larger than their boundaries and because the titanium cations in the APDs order themselves in such a way as to give those regions a stronger magnetic moment.

Beyond this, however, the researchers know little. How the two regions interact with one another, for instance, is still a nagging theoretical question.

While they may not know the details of the interaction, the scientists do have an idea of the kinds of conditions in the laboratory that might persuade a titanohematite sample to self-reverse. Lawson and Nord, working with synthetic samples, have shown that the occurrence of self-reversals depends on the sample's composition and thermal history. When minerals of certain compositions are heated to high temperatures (above the point at which an ordered distribution of cations becomes disordered) and then rapidly cooled, or quenched, they become self-reversing. Lawson thinks this is because the cations are not given enough time to sort themselves into a completely ordered pattern. Instead, APDs and their boundaries are "frozen" in place by quenching.

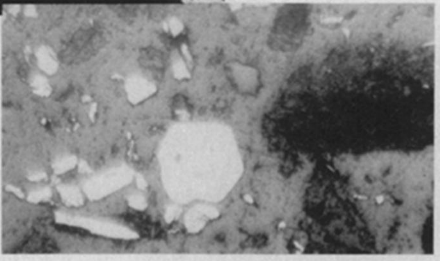
According to Robert Hargraves at Princeton (N.J.) University, self-reversing titanohematites of other compositions have been found in natural rocks that also contained magnetite polarized parallel to the earth's field. When researchers heated up and then cooled these titanohematites in the laboratory, however, they were unable to make the minerals self-reverse. Hargraves and Lawson believe that these minerals were originally cooled in nature over a very long time — on the order of millions of years. So, for certain compositions, slow cooling caused titanohematites to separate out of the mixture.

While it is nearly impossible to duplicate nature's slow cooling process in the laboratory in order to test these ideas, Hargraves and Lawson are both working on ways to learn more about the minerals. They are motivated in part by the conviction that in igneous and metamorphic rocks, titanohematites, which are more stable than magnetite, may be far more important to paleomagnetic studies than their minor abundance might suggest.

"The scatter and uncertainties in the paleomagnetic data are very considerable, allowing radically different interpretations of the body of data," says Hargraves. "I believe that the resolution and clarification of some of the big earth science problems pertaining to the motion of the plates require good paleomagnetic data.... And some of the complexity which we are now beginning to recognize in the magnetic record may be caused by the presence of this material."

—S. Weisburd

Butler



Titanohematite, rather than magnetite, is the dominant magnetic mineral in the San Juan Basin; rocks shown at left are at the basin's Angel Peak. Below, a hexagonal grain of titanohematite, 15 microns wide, sits in the center of a photomicrograph of a polished grain from the basin sediments.

property of the lava flow as it is trying to seek its way to the surface of the earth, he says.

The issue is important because it speaks to the ultimate usefulness of titanohematites as a geochemical tool for unearthing the chemical and physical history of magmas as they flow from depth to the surface. As yet, however, Champion has been unable to interest volcanologists. "If we could make some necessary association that tells them something about their [volcanic] system merely by identifying this mineral, then they'd be damn interested," he says. "But that remains to be shown."

One possible reason for the relatively few findings of self-reversing minerals in lava beds may be that these kinds of rocks are very easy to erode, says Robert F. Butler at the University of Arizona in Tucson. Butler and Everett H. Lindsay will soon publish a paper in THE JOURNAL OF GEOLOGY describing their discovery of titanohematite in 750 meters of sediment, representing about 15 million years of erosion deposits, in the San Juan Basin in New Mexico. These 70-million-year-old sediments are reported to contain virtually no magnetite. And in the northwest corner of Wyoming, the paleomagnetists have also found waves of titanohematite flooding sedimentary sections of the Big Horn Basin, where some magnetite is present but only in extremely small amounts. "It seems odd to people that we would have this family of minerals that we have become accustomed to thinking are very rare and now they seem to be turning up as the major magnetic constituent in some rather important sedimentary basins in North America," says Butler. "And these sediments I'm looking at seem to be the eroded counterparts of the kind of volcanic rocks that Duane [Champion] is seeing."

Easy erosion would also account for the fact that Butler has yet to find traces of the volcanos from which the titanohematites might have originated, even though other volcanic fields of about the right age have been found.

Butler and Champion believe that the titanohematite sediments in the Rocky Mountain region do have a direct volcanic origin and that they came from one volcano. They speculate that titanohematites formed in the magma from this volcano — as well as from those at Mt. Shasta and Mt. Haruna — because the magma had to eat its way up through preexisting continental crust and in so doing perhaps had its chemistry altered. In the San Juan Basin, for example, sediments were deposited after the Rocky Mountains were created in the collision of an oceanic plate with North America, an event called the Laramide orogeny. The pulling down (subduction) of the oceanic plate beneath North America is thought to have caused increased volcanic activity. This means that the "Bunsen burner" marched farther inland than usual, says Champion. Magmas came up through granite and other kinds of Precambrian basement rocks, and in the process may have been adjusted in some way so that they came out of the earth bearing titanohematites.

"If we're anywhere near correct about the origin of these minerals, then any of these basins that have a significant amount of their sediments derived from volcanic rocks should have a significant amount of self-reversing minerals in them," adds Butler. Next summer, he plans to study other Laramide basins in North America to see if the same kind of self-reversers show up there as well. Champion, too, is planning to hunt for titanohematites in lava flows from other explosive volcanos such as the 12,000-year-old bed near Glacier Peak in Washington.

"I'm guessing that in the greater scheme of things, self-reversing minerals are still rare. They're just not as rare as we thought," he concludes. "But I don't think we know. And nobody's looking for them because I don't think anyone believes they're out there." □

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