Epitaxial Study of Meteorite ALH84001 Reveals Magnetite Crystals Intergrown with Carbonates at >120°C

Using transmission electron microscopy (TEM), a research team discovered that magnetite crystals in the meteorite known as ALH84001 (previously identified as originating on Mars) were atomically intergrown with the surrounding carbonates by a rigorous form of epitaxy. According to the researchers, the resulting complementary orientation of crystals means the magnetites and carbonates must have grown simultaneously at temperatures much greater than 120°C. They said that the implied high-temperature origin virtually eliminates the possibility that fossilized Martian organisms exist in this meteorite, disputing previous reports of forms consistent with nanofossils.

According to the current research published in the July issue of *Meteoritics and Planetary Science*, epitaxy can occur if two similarly patterned lattice planes of crystal structures are parallel. Previous studies have shown that the ideal lattice "misfit" between two crystal structures should not exceed 15%. In this case, the lattice misfit was only 11–13%, which is ideal for epitaxial growth, according to the researchers.

Many of the epitaxially formed magnetite whiskers in the meteorite appear to be free of internal defects, the researchers said. Such is typically the case of crystals formed at elevated temperatures, while those grown at lower temperatures tend to have high densities of internal defects. Also, the researchers found epitaxially formed magnetite crystals in mineral specimens from volcanoes in Indonesia and Alaska. These crystals formed at temperatures in excess of 600°C, the researchers said. They compared these to the magnetites in the meteorite because volcanoes also exist on Mars. According to John Bradley, an adjunct professor of Materials Science and Engineering in the Georgia Institute of Technology and executive director of MVA Inc., a microanalytic company in Norcross, Ga, the comparison provided further evidence of a high-temperature origin.

This article is the third in a series of Bradley's technical papers reporting research accomplished with Hap McSween of the University of Tennessee—Knoxville and Ralph Harvey of Case Western Reserve University. In their first paper, published in 1996 in *Geochimica et Cosmochimica Acta*, the researchers used TEM to discover that elongated forms in the meteorite contained crystallographic screw dislocations, typically formed during high-temperature vapor-phase growth. In 1997, their article in *Nature* showed what the researchers believed to be inorganic mineral lamellae.

Bradley said, in reference to another research teams's hypothesis that the meteorite contains nanofossils, indicating life on Mars, "There are really two debates here—whether there is evidence of life in this meteorite and whether life exists on Mars."

Reptation Model of Polymer Behavior Confirmed

Researchers at the University of Delaware (UD), the University of Alabama—Birmingham, and the National Institute of Standards and Technology published a report in the July 28 issue of *Macromolecules* that confirms a scientific theory of polymer behavior known as the "reptation model." The reptation theory, proposed in 1971 by Nobel Prize recipient Pierre-Gilles de Gennes, holds that hot polymer chains coil back and snap forward, snakelike, rippling a "signature" wherever plastics are joined together. According to UD doctoral candidate Keith A. Welp, lead author of the current article, over the past 27 years researchers have challenged the model by arguing that polymer chains act in tandem with nearby molecules and, therefore, exhibit far more complex behaviors in hot environments.

To learn how polymer chains move when plastic components are welded together, the research team first "labeled" two types of polystyrene molecules. In the middle section of some chains, they replaced 50% of the molecules' hydrogen atoms with deuterium. Mirror-image molecules were then created by replacing hydrogen with deuterium on both ends, without disturbing the middle of the chain.

Labeling polystyrene with deuterium helped the researchers track the chains' movement during welding. Just as the end of a rope thrashes more freely than its center, Welp said, the exposed head and tail of a polymer chain exhibit greater flexibility. In experiments, more deuterium wound up on one side of a welded seam. The researchers attribute this to the confined, deuterium-loaded midsections of half the chains that stayed on one side, while the flapping, deuterium tips of the mirror-image molecules jumped across the interface. An experimental interface was created by spreading the hydrogen-deuterium-hydrogen (HDH) chains onto a platform of silicon, then covering clean, glass slides with the deuterium-hydrogen-deuterium (DHD) chains. Sliding the DHD samples carefully into water helped dislodge them from the glass so that the researchers could ease them directly on top of the HDH layer. They then evaporated the water and heated their samples before investigating the molecular characteristics of the resulting weld.

The researchers subjected the welded samples to two types of tests: specular neutron reflectivity measurements to reveal the location of deuterium and dynamic secondary ion mass spectroscopy to trace the "smooth, rippling pattern" of deuterium atoms left by the snakelike motion of polymer chains.

High-Temperature, High-Pressure Perovskite Studies Suggest Anomalous Properties of Earth Mantle

Researchers from the Max Planck Institute for Chemistry in Mainz, Germany studied the stability and solidus of materials relevant to the lower mantle of the Earth at very high pressures and temperatures to help explain seismic measurements. Their observations reveal several anomalies in the lowermost part of the Earth´s mantle: a discontinuous increase in velocity about 200 km above the core-mantle boundary and an ultralow velocity zone in the very near vicinity of the core. While the first observation has been interpreted as being due to a possible breakdown of the major lower-mantle constituent $(Mg,Fe)SiO_3$-perovskite to its component (Mg,Fe)O and a dense form of SiO_2, the second observation has been interpreted to be due to partial melting.

The breakdown of perovskite not only requires that the resulting mineral assemblage is denser than that of perovskite, it would also result in significant changes in the chemical and rheological properties of the deep mantle. Partial melting would require a melting behavior that is in contrast to previous melting experiments on the major lower-mantle components and traditional knowledge of the eutectic behavior observed at low pressure.

R. Boehler, G. Sergiou, and A. Zerr of the High Pressure Group at Max Planck have examined the stability of perovskite by heating stoichiometric mixtures of (Mg,Fe)O and SiO_2 in a diamond anvil cell with a high power CO_2-laser to about 3000 K in a hydrostatic medium at pressures up to 100 GPa. This technique avoids both large pressure and temperature gradients which is an essential requirement for a reliable assessment of the stability of solids, especially under extreme conditions. In all experiments, as published in the June 26 issue of *Science*,

$(Mg,Fe)SiO_3$-perovskite was formed which unambiguously shows that this phase is stable under lower mantle conditions. Moreover, both $MgSiO_3$ crystal and glasses subjected to similar conditions also formed perovskite as a single phase, as evident from Raman spectra. No SiO_2 was detected. Furthermore, the fluorescence spectra of chromium(III)-doped perovskite were recorded at analogous conditions, which in the case of decomposition would produce a strong fluorescence line of $MgO:Cr^{3+}$. No MgO was detected. According to the researchers, these results indicate that decomposition of perovskite in the lower mantle is highly unlikely and is not the cause for unusual seismic patterns.

In another study, published in the July 10 issue of *Science*, the same authors investigated the solidus of the mantle's relevant material to about 60 GPa (equivalent to the 1500 km depth inside the Earth); in earlier examinations the solidus was constrained to about 25 GPa (equivalent to about 700 km depth). The small samples of multicomponent material (70 μm × 70 μm × 15 μm) embedded in the argon pressure medium were heated using CO_2-laser radiation in a diamond anvil cell. Changes in the texture on the recovered sample surface were used to verify partial melting of the sample material using a scanning electron microscope (SEM) and an atomic force microscope (AFM). This new approach of the melting temperature determination at high pressures in a diamond anvil cell is usable for any one- or multicomponent material, especially if no other signs of melting (for example change in the absorption of the heating laser radiation) can be used. The results show that the melting temperature of the multicomponent material studied is significantly lower than the melting temperatures of its end-members' phases. Even though the solidus in the deep mantle lies over 1500 K above the average present-day geoterm, its value at the core-mantle boundary (CMB) approaches the outer core temperature. Thus, according to the researchers, partial melting of mantle material close to the outer core may explain observed seismic anomalies in this region.

According to the researchers, the solidus of multicomponent mantle material is the key parameter in modeling the early Earth. It is possible that after the Earth´s formation a significant part of the Earth was at least partially molten. Even the presence of a small amount of melt results in a significant weakening of mantle material. Moreover, they said, the temperatures at which mantle materials solidify marks a change in the character of convection features during the Earth's evolution.

Chemical Composition of Siberian Basalt Suggests Ancient Deep Eruptions

Researchers at the University of Rochester and Harvard University have gained new knowledge of the underpinnings of catastrophic eruptions on Earth causing mass extinction by analyzing the chemical composition of lava disgorged in one such massive period of volcanism in Siberia 250 million years ago. The findings by geochemists Asish Basu, Robyn Hannigan, and Stein Jacobsen, published in a recent issue of *Geophysical Research Letters*, indicate that the lava that erupted at the time arose from the pristine lower mantle. By studying the lava's major chemical components, such as sodium, magnesium, and iron, as well as rare isotopes of neodymium, strontium, lead, and

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helium, the authors have found that the chemical composition of the Siberian flood basalts, the vast expanses of rock that result from such volcanic outpourings, matches that of magma found deep within the Earth.

The team analyzed rocks culled from the Siberian flood basalt for compounds that are rare on the Earth's surface but common in parts of the lower mantle that is believed to have originated soon after the birth of the solar system. They also drew upon experiments conducted at other institutions where researchers melted rocks in the laboratory, much as happens deep within the Earth's interior. They found that the Siberian flood basalt arose from superheated, buoyant rock that rose in a narrow column from a depth of 1,800 miles into a mushroom-shaped mass of hot rock just 40 to 50 miles below present-day Siberia. Then, according to the researchers, some 250 million years ago, 12–16% of this rock suddenly melted and broke through the Earth's crust, resulting in a vast flood of lava. Scientists believe this particular volcanic outpouring played a role in mass extinction in which up to 95% of all plant and animal species were killed.

"It is surprising that most of this melting occurred so close to the Earth's surface, really just beneath the crust," said Jacobsen, a Harvard professor of geochemistry. According to the researchers, while it is easy to envision rocks melting in the massive crucible at the Earth's core, the lava that spilled into Siberia 250 million years ago melted at the much lower temperatures and pressures found just beneath the surface. Basu, a professor of earth and environmental sciences at Rochester, said that it is an example of decompressional melting in which a large decrease in pressure can depress the melting point of a substance.

The work is the latest in a series of findings by Basu and other geologists that point to the lower mantle as the source of such volcanism in Siberia and other parts of the world. Three years ago, Basu and colleagues published an article in *Science* which suggested that the presence of an unusual concentration of helium-3, an ancient gas common deep within the Earth, could serve to trace the Siberian flood basalt's lineage to the lower mantle.

Scientists have long debated whether flood basalts have their origins in rumblings deep within the Earth or closer to its surface. According to Basu, some scientists discounted the helium-3 theory, suggesting that the material may have been recycled from cosmic dust falling to Earth and making its way into the rocks. According to Basu, the current research indicates that "the lava that's now hardened into the Siberian flood basalt originated far beneath the Earth's surface, between the lower mantle and the molten iron core."

Fabricated Coatings Mimic Structure of Nacre

The process of synthetically fabricating the nacre of abalone shells, a coating composed of alternating layers of aragonite and a biopolymer, has eluded scientists who find value in the strength, hardness, and toughness of this material. Researchers from Sandia National Laboratories and the University of New Mexico have reported in the July 16 issue of *Nature* a "self-assembly process for preparing nanolaminated coatings that mimic the structure of nacre." Their process is based on the tendency of two-sided detergent molecules, composed of hydrophilic and hydrophobic portions, to spontaneously form micelles. In the composite process, micelles separate and orga-

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nize inorganic molecules around the micelles' hydrophilic exterior and organic molecules within the hydrophobic interiors. During the coating process, the intentional evaporation of water further arranges the micelles into alternating layers of organic and inorganic molecules in one step. A low-temperature heat treatment polymerizes the organic and inorganic layers and bonds their interfaces.

The researchers heated TEOS ($Si(OCH_2CH_3)_4$), ethanol (EtOH), water, and dilute HCl (mole ratios: 1 : 3.8 : 1 : 5×10^{-5}) at 60°C for 90 min. They diluted the sol with ethanol (1 : 2), then added water and dilute HCl. A coupling agent was added followed by surfactant, monomer, crosslinker, and initiator. The final reactant mole ratios were "1 TEOS:22 EtOH:5 H_2O:0.004 HCl:0.21 surfactant:0.16 DM:0.02 HDM:0.08 OTS:0.02 initiator." The researchers then deposited the coatings on (100)-silicon by dip-coating. The coatings were then heated or irradiated with ultraviolet light to initiate organic polymerization.

The researchers said that their process differs from other nanocomposite self-assembly processes because they covalently link the organic and inorganic interface in a rapid (~10 s) dip-coating continuous process.

Sonochemical MoS_2 Demonstrates High Catalytic Activity

Using high-intensity ultrasound, researchers at the University of Illinois at Urbana-Champaign have discovered a catalyst for removing sulfur-containing compounds from gasoline and other fossil fuels. The catalyst is a new form of molybdenum disulfide. Molybdenum disulfide normally consists of long, flat layers of molybdenum metal atoms sandwiched above and below by single atomic layers of sulfur. It is used commercially as a catalyst to remove sulfur-containing compounds in gasoline. Upon combustion, these unwanted sulfur compounds would contribute to the formation of acid rain. Kenneth Suslick, professor of chemical sciences, said that the flat planes interfere with the material's ability to react with fuels to remove sulfur. He said, "This is because all the reactions necessary for sulfur removal occur along the edges of the long planes, and the bigger the planes, the less relative edge there is."

Suslick and students Millan Mdleleni and Taeghwan Hyeon use sonochemistry to make molybdenum disulfide with many more edge atoms. The sonochemical synthesis arises from acoustic cavitation. According to the researchers, the collapse of these cavitating bubbles generates intense local heating, forming a hot spot in the cold liquid with a transient temperature of about 9,000°F, a pressure of about 1,000 atmospheres, and the duration of about 1 ns.

Suslick said that when the bubbles collapse, the vapor of volatile molybdenum-metal-containing compounds inside the bubbles is decomposed into hot metal atoms. These atoms then react with sulfur dissolved in the liquid to form clusters of MoS_2. As reported in the June 24 issue of the *Journal of the American Chemical Society*, the clusters of spherical particles are on the average 15 nm in diameter. He said that these clusters are too small to have extended planes of atoms and consequently possess many more edge atoms that can participate in the sulfur-removal process. After testing MoS_2 prepared sonochemically and conventionally with sonochemical Mo_2C, commercial ReS_2, and RuS_2, the researchers conclude that sonochemically prepared MoS_2 is 10 times more active than the standard industrial catalyst.

Solid, Metal-Bearing Precursors Create Ceramic Parts Without Shrinkage or Change in Shape

Researchers at Ohio State University have developed a technique for creating near net-volume ceramic parts for high-tech devices. The process of sintering often shrinks ceramic parts nonuniformly, which causes them to deform and develop cracks. Ken Sandhage, associate professor of materials science and engineering, said, "Ceramics used in a number of advanced devices won't work well unless they conform to exactly the right size and shape." Sandhage's solution to this problem is to start the manufacturing process with a precursor that consists of a mixture of ceramic and metal powders

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instead of with just ceramic powder.

Upon firing in air or oxygen, the metal powders oxidize and become ceramics. Sandhage said, "We figured that if we started with a precursor that contained some alkaline earth metals, which shrink, and some nonalkaline earth metals, which expand, then we could tailor the composition so that the net volume change when we fired the mixture would be zero."

According to their article published in the May 1998 issue of *Journal of Materials Research*, the researchers mechanically alloyed and uniaxially pressed three types of solid, metal-bearing precursors: Ba–Al_2O_3–Si–SiO_2 (BASS), Ba–Al–Al_2O_3–SiO_2 (BAAS), and Ba–Sr–Al–Al_2O_3–SiO_2 (BSAAS). They then placed the three types of specimens on alumina substrates and annealed through a series of heat treatments, beginning at 300°C, in an O_2/N_2 gas mixture. Conversion of the BAAS specimen occurred at 1350°C, and at 1500°C for the BASS specimen and 1200°C for the BSAAS specimen. The ceramic disks retained the precursor shape, dimensions, and relative density. The researchers found that the differences in the initial and final diameters were less than 0.7%.

The metals in the precursor provide additional benefits. Because they bind the ceramic powder together, they eliminate the need for traditional organic binding materials such as carbon. Manufacturers normally burn these organic materials from the final ceramic, which releases hydrocarbons into the atmosphere and leaves pores in the material.

Also, the lack of organic material in the precursor means that the process can produce certain ceramic compounds at lower temperatures, which saves energy. The researchers have produced ceramic compounds at temperatures as low as 300°C, well below half the temperature normally required. The research team also dispersed sources of oxygen within the shaped precursor so that the metal would oxidize faster. While this reaction works at higher temperatures—900°C—it is capable of producing larger ceramic parts within a few hours.

Sandhage's research team has also used such processing to fabricate shaped ceramic composites. For these materials, some of the metal in the precursor is left unoxidized. For some applications, such residual metal can enhance the electrical conductivity, thermal conductivity, or toughness of the part.

Birefringent Neutron Tunneling Waves Observed in Magnetic Films

Scientists at the Max-Planck-Institut für Metallforschung in Stuttgart found that when a neutron hits a wall and is reflected, the neutron tunneling wave traveling below the surface is split into two components whenever the medium is magnetic. Neutrons with thermal energies are used in solid-state physics to investigate structural, magnetic, and dynamic properties of

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bulk materials. The interaction of neutrons with matter is twofold since they carry a magnetic moment and experience both nuclear and magnetic potentials. However, these interactions are small, and the depth in which information can be gained in a scattering experiment is typically in the order of centimeters. Therefore, according to the report, the researchers used the quantum-mechanical tunneling effect in order to create an exponentially decaying wave traveling in a skin a few nanometers thick. Tunneling states inside the medium can be observed via Bragg reflection at lattice planes lying perpendicular to the surface; the diffraction process represents only a small perturbation of the neutron state.

When the researchers carried out an experiment on a thin iron film at the high flux reactor of the Institute Laue-Langevin in Grenoble, France, an unpolarized neutron beam was directed onto the surface of the film under grazing incidence, and the neutron tunneling state beneath the surface was found to be split into two components whenever the film was magnetized. The splitting of the beam, due to the Zeeman effect induced by the magnetic potential of the film, was found to be very sensitive to small magnetic stray fields of nanometer dimensions. According to the researchers' report in *Physical Review Letters* **81** (1998), the fundamental effect of birefringent tunneling can therefore be applied to study subtle magnetic phenomena in magnetic thin films and interfaces of technological interest. □

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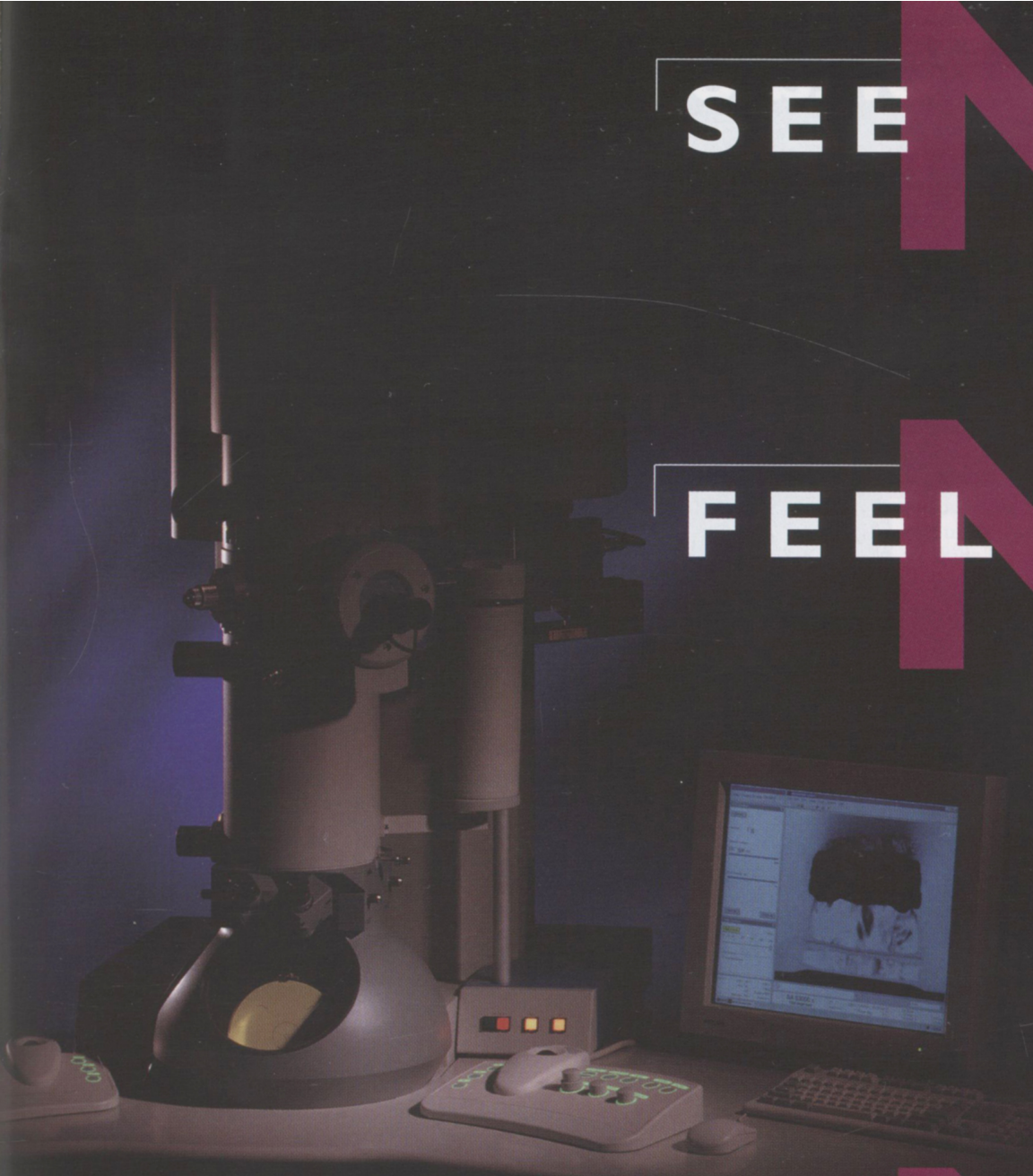

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