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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/346/6213/1096/suppl/DC1 Materials and Methods Supplementary Text Figs. S1 to S9 Tables S1 and S2 References (30-36) Movies S1 to S7 14 April 2014: accepted 24 October 2014 10.1126/science.1254787

MINERALOGY

Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite

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Meteorites exposed to high pressures and temperatures during impact-induced shock often contain minerals whose occurrence and stability normally confine them to the deeper portions of Earth's mantle. One exception has been MgSiO₃ in the perovskite structure, which is the most abundant solid phase in Earth. Here we report the discovery of this important phase as a mineral in the Tenham L6 chondrite and approved by the International Mineralogical Association (specimen IMA 2014-017). MgSiO₃-perovskite is now called bridgmanite. The associated phase assemblage constrains peak shock conditions to ~ 24 gigapascals and 2300 kelvin. The discovery concludes a half century of efforts to find, identify, and characterize a natural specimen of this important mineral.

n the geosciences, the complexity of compositions and histories of naturally occurring minerals and rocks provides an important ground truth against which experiment and theory are measured. One of the most glaring omissions in the study of Earth's mantle has been the

inability to find naturally occurring specimens of what we believe to be Earth's most abundant rockforming phase, (Mg,Fe)SiO₃ in an orthorhombic ABO₃ perovskite structure. Despite appearing for decades in numerous experimental and theoretical studies (1-5), characterizations of possible natural samples have not been sufficient to meet International Mineralogical Association criteria for naming a new mineral (6). Consequently, any detailed chemical, structural, and petrographic analysis of natural (Mg,Fe)SiO₃-perovskite has remained impossible. In addition, having a formal mineral name for a phase that is so important is important in itself. Various ambiguous or incorrect terms such as "silicate perovskite" and "perovskite" have been used for describing this phase, but they convey ambiguity to the description of research findings. We put this ambiguity to rest by describing the natural occurrence of bridgmanite: MgSiO₃ in the orthorhombic ABO₃ perovskite structure. The name bridgmanite honors Percy W. Bridgman (1882-1961), the 1946 Nobel laureate in Physics, for his fundamental contributions to high-pressure mineralogy in particular, and to high-pressure research in general.

The importance of bridgmanite in the lower mantle of Earth has long been recognized: Several lines of evidence show that it forms through a

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Fig. 1. Scanning electron microscope image of a bridgmaniteakimotoite aggregate. The backscatter electron image reveals an aggregate of submicrometer-sized crystals of bridgmanite and akimotoite enclosed in (Mg,Fe)SiO₃ glass and within a Tenham shock-melt vein. Majorite is found in the vein matrix. The bridgmanite-akimotoite clast is a pseudomorph after pyroxene that was trapped in the melt. This observation is consistent with an earlier report about the possible occurrence of bridgmanite with akimotoite in Tenham (16).



breakdown of rock-forming $(Mg,Fe)_2SiO_4$ into (Mg,Fe)O periclase and $(Mg,Fe)SiO_3$ bridgmanite in the lower mantle of Earth below a depth of 660 km (*I*-5). Bridgmanite remains stable to the D" layer, nearly down to the core-mantle boundary region at a depth of 2900 km (7). Thus, bridgmanite makes up about 38 volume % of the entire Earth (4). The chemical and physical properties of bridgmanite have a large influence on elemental distribution, mass flow, and heat flow within Earth's mantle. Numerous efforts have all failed to find a naturally occurring example of this elusive mineral for several reasons. Most im-

el. Intensity (a.u.)

Fig. 2. Powder diffraction pattern and Rietveld refinement of bridgma-

nite. The figure shows the observed diffraction pattern (black line and symbols) of bridgmanitebearing shock-melt vein material in thin section USNM 7703 (23), whole pattern refinement (red), refined pattern of bridgmannite (blue), residual of fit (green), and positions of observed reflections of bridgmanite, akimotoite, and ringwoodite (blue, red, and green tick marks, respectively). The x-ray wavelength was 0.3344 Å. The weighted-profile refinement factor was

portantly, (Mg,Fe)SiO₃ in the perovskite structure is stable only at very high pressures and temperatures (β). The mineral is metastable under ambient conditions but vitrifies above temperatures as low as 310 K (β). The exhumation of rocks originating in the lower mantle is far too slow to permit the preservation of terrestrial bridgmanite, although inclusions in some diamonds from such rocks have been interpreted as the breakdown products of bridgmanite (IO, II). Heavily shocked meteorites provide an alternative route for preserving bridgmanite. Pressures and temperatures during the shock event can be high



0.08, and there were 799 observations. The examined portion of the Tenham meteorite revealed diffraction by bridgmanite, akimotoite, and ringwoodite in relative volume proportions of 11, 16, and 74%. Ringwoodite forms clasts within the shock-melt vein (fig. S1), some of which occur beneath the examined akimotoite-bridgmanite-glass clast (the x-ray beam covers a 3 × 4 μ m² area but it passes through the entire ~30– μ m-thick rock section). The bridgmanite-akimotoite aggregate has a volume proportion ~ 0.7:1, in accord with scanning electron microscope examination. rel., relative; a.u., arbitrary units.

Fig. 3. Correlation of unit cell volume with Fe content in synthetic and natural bridgma-

nite. Bridgmanites with dominantly ferrous iron exhibit a weak increase in volume with increasing iron content [dashed curve (24)]. Bridgmanites with large concentrations of ferric iron (24, 63) exhibit a more pronounced increase of volume with increasing Fe content (squares). Natural bridgmanite ranges in cell volumes due to chemical variations (fig. S2) as



indicated by the hached region. However, the average volume of natural bridgmanite from Tenham lies on an extension of the trend established by synthetic ferric bridgmanite. The black vertical bar indicates an approximate uncertainty for the volume measurements on synthetic bridgmanite based on the singlecrystal diffraction studies of the Mg end member at ambient pressure (63–66). pfu, per formula unit. enough to stabilize bridgmanite, and the release to ambient conditions may be sufficiently fast to kinetically inhibit breakdown reactions. As a result, several high-pressure phases known to be stable only deep within Earth's mantle have been found as minerals in these meteorites (12-18). These observations instigated decades of efforts to find and characterize bridgmanite in shocked meteorites (15-19). Meticulous transmission electron microscopy examination yielded indications of the presence of bridgmanite in chondritic and martian meteorites (15-19). However, rapid vitrification in the electron beam, a lack of adequate sets of reflections for unique crystallographic indexing, and the absence of quantitative structure factor moduli rendered these observations insufficient to characterize a new mineral.

A different approach to the search for bridgmanite lies in using microfocused high-energy synchrotron x-ray beams instead of electron beams for diffraction. The intense high-energy x-ray beam does little to damage bridgmanite because of its low absorbance. Micro-focusing and novel fast readout area detector techniques permit efficient mapping of possible host regions in shocked meteorites (20). Our search focused on shock-melt veins and their inclusions, which were previously identified as the hosts of other high-pressure silicate phases (12-20). In particular, we examined the highly shocked Tenham L6 chondrite and identified bridgmanite in clasts within the shock-melt veins. We found bridgmanite always associated with akimotoite but never as isolated crystals in the melt vein. These two phases along with a vitreous matrix whose composition is identical within error to that of the bridgmanite (table S1) replace precursor orthopyroxene crystals trapped within a melt vein (Fig. 1 and fig. S1). We interpret this assemblage to reflect bridgmanite that partially vitrified upon release from the shock state on the parent body or during its residence on Earth after its fall in 1879. We hypothesize that the volume expansion upon transformation from bridgmanite or dense glass into normal glass by ~ 33% (21) and 1 to 2% (22), respectively, induces stresses in the surrounding rock that help preserve the remaining bridgmanite.

Bridgmanite assumes the Pnma perovskite structure with unit cell parameters $a = 5.02 \pm$ 0.03 Å, $b = 6.90 \pm 0.03$ Å, and $c = 4.81 \pm 0.02$ Å, which yield a unit cell volume of 167 ± 2 Å³ (Fig. 2) (23). The uncertainties (± SEM) are from (i) uncertainty in the Rietveld refinement (see Fig. 2) and (ii) variations in cell parameters due to varying chemical composition (fig. S2). Akimotoite and ringwoodite also contribute to the diffraction pattern. The average composition of the type material (table S1) has a formula unit of (Mg_{0.75}Fe_{0.20}Na_{0.03}Ca_{0.02}Mn_{0.01})Si_{1.00}O₃ (23). The composition is well within the range of synthetic bridgmanites, despite being a quite sodic and Ferich composition in comparison (fig. S2).

The cell volume of natural bridgmanite lies on an extension of the trend of volume expansion along with increasing Fe^{3+} content (24), which is consistent with a large amount of ferric iron as compared to synthetic bridgmanites (Fig. 3). As noted above, the holotype specimen of bridgmanite also contains high concentrations of Na. This may extend the stability field of bridgmanite (25) and supports charge balance for ferric iron via Na-Fe³⁺-coupled substitution in holotype bridgmanites at redox conditions below the iron-wüstite buffer (26), but plausibly also in the terrestrial and martian (27) lower mantles.

The evaluation of the shock conditions in Tenham beyond the examination of plausible recovery paths for bridgmanite is outside the scope of this study. The strict association of akimotoite and bridgmanite and the likely absence of bridgmanite in the matrix of the shockmelt vein are pivotal to an assessment (fig. S3). They suggest that the peak pressure exceeded 23 GPa, with temperatures in the melt exceeding the solidus at ~2200 K. The absence of bridgmanite as isolated crystals within the shock-melt vein suggests that pressures were too low to permit crystallization from melt. Using these constraints, we estimate the conditions of formation of bridgmanite in Tenham to be 23 to 25 GPa and 2200 to 2400 K (fig. S3). This estimate is consistent with a more recent estimate by Xie et al. (20) based on observation of vitrified bridgmanite. The occurrence of bridgmanite along with conditions of formation of other highpressure minerals imposes strong constraints on pressure and temperature conditions during highlevel shock events in meteorites.

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SUPPLEMENTARY MATERIALS

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CHEMICAL OCEANOGRAPHY

Increasing anthropogenic nitrogen in the North Pacific Ocean

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The recent increase in anthropogenic emissions of reactive nitrogen from northeastern Asia and the subsequent enhanced deposition over the extensive regions of the North Pacific Ocean (NPO) have led to a detectable increase in the nitrate (N) concentration of the upper ocean. The rate of increase of excess N relative to phosphate (P) was found to be highest (~0.24 micromoles per kilogram per year) in the vicinity of the Asian source continent, with rates decreasing eastward across the NPO, consistent with the magnitude and distribution of atmospheric nitrogen deposition. This anthropogenically driven increase in the N content of the upper NPO may enhance primary production in this N-limited region, potentially leading to a long-term change of the NPO from being N-limited to P-limited.

he rate of deposition of reactive nitrogen (i.e., $NO_y + NH_x$ and dissolved organic forms; see supplementary text S1) from the atmosphere to the open ocean has more than doubled globally over the past 100 years (1), reaching a magnitude that is comparable to about half of the global ocean N_2 fixation (2). The increase in atmospheric nitrogen deposition (AND) is particularly acute in the North Pacific Ocean (NPO) due to rapid population growth and burgeoning industrial activity in northeast Asian countries. These changes in northeast Asia have markedly increased reactive nitrogen fluxes in the adjacent marine environment (3, 4), largely through atmospheric transport by westerly winds and subsequent deposition. Though it has been recognized that such an increasing addition of

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reactive nitrogen to the ocean could lead to major changes in the upper ocean nitrogen cycle and biological productivity (5), the majority of studies conducted to date have suggested that the impact is small and not detectable (1), except in near-shore environments and marginal seas (3). A recent study directly comparing nutrient measurements made over more than two decades showed that nitrate (N) concentration has increased in the northeast Asian marginal seas and that this increase was probably due to strongly growing AND (3). Here we extend this analysis to the entire NPO and show that the anthropogenic influence has already affected the open-ocean nitrogen cycle.

Owing to a lack of basin-wide, nutrient concentration data of sufficient duration (decades) at strategic locations, we reconstructed the temporal changes in N across the NPO using a method based on the relation between the excess of N in a water parcel relative to that expected based on the phosphate (P) concentration and the chlorofluorocarbon-12 (CFC-12)-derived ventilation age of that water parcel (6) (supplementary text S2). The excess in N relative to P—i.e., N^* (7, 8)—at each sampling location was calculated as: $N^* = N - R_{N:P} \times P$, where N and P are the measured concentrations and $R_{N:P}$ is the Redfield ratio of 16:1. Because of increasing

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EARTH SCIENCE

Bridgmanite-named at last

The most abundant mineral in Earth's interior gets a name

By Thomas Sharp

he most abundant solid phase in Earth's interior, making up 38% of Earth's volume, is magnesium iron silicate (Mg,Fe)SiO₂. This material is known to form a perovskite structure. However, no samples of the mineral can be obtained from Earth's lower mantle; without a well-characterized natural sample, it has not been possible to formally name the mineral. On page 1100 of this issue, Tschauner et al. (1) use synchrotron micro-x-ray diffraction and electron probe microanalysis to determine the crystal structure and composition of natural (Mg,Fe)SiO3-perovskite in a shocked L chondrite (a stony, low-iron meteorite). They name it bridgmanite, after the father of high-pressure experiments, Percy W. Bridgman (1882 to 1961).

A mineral is a naturally occurring crystalline solid with distinct, but not fixed, chemical composition. According to the commission on new mineral names, one must characterize the structure and composition of a natural sample to give it a mineral name. Previous reports of natural MgSiO₃-perovskite have shown that it can occur in shocked meteorites (2, 3), but in both cases, the material was damaged by irradiation during transmission electron microscope analysis, and the structure had not been well characterized. Tschauner *et al*.'s careful characterization finally allows this important mineral to be named.

Earth scientists know the physical structure of the deep Earth mainly from seismic studies, which have shown that seismic velocities change suddenly at particular depths. These seismic discontinuities show that Earth has a layered structure consisting of a solid inner core, a liquid outer core, a lower mantle, and an upper mantle (see the first figure). To determine which solid materials make up these layers of the inner Earth, we need to know how Earth's materials react to extreme pressures and what structures are stable under the extreme conditions of pressure and temperature within Earth (4). This information is gained from a combination of high-pressure experiments, thermodynamics, and modeling studies, with important confirmation from natural samples, usually (although not always) from meteorites.

High-pressure experiments use devices such as the diamond-anvil cell (DAC) and the multi-anvil apparatus to generate the extreme pressures of planetary interiors. The groundwork for these experiments was laid by Bridgman. More than 100 years ago, he invented a high-pressure apparatus and pressure seal that solved the problem of sample containment (5). With this press, Bridgman was able to compress materials to 7000 atmospheres (atm). By incorporating first a hydraulic press and then carbide anvils, he could eventually reach pressures of 50,000 to 100,000 atm (5 to 10 GPa) (6). Bridgman's opposing-anvil design with a cylindrical gasket led to the development of the DAC, which has allowed mineral physicists to reproduce the conditions found in the deep Earth and other planetary interiors (4).

The combination of experimental mineral physics, thermodynamics, and first-principal theory has provided a detailed model of the inner Earth that is consistent with geophysical observations and a bulk-earth chemistry resembling that of chondrites (see the first figure). High-pressure experiments provide a direct means of determining the stabilities of various structures as a function of pressure, temperature, and composition, as well as physical properties such as elasticity. From mineral physics, we know that the upper mantle consists of familiar minerals such as olivine, pyroxenes, and garnet. However, in the mantle transition zone, higher-density spinel and garnet structures predominate. In the lower mantle, the even denser perovskite and rock-salt structures are stable. Bridgmanite (perovskite structure) differs from upper mantle and crustal minerals in that silicon fills octahedral rather than tetrahedral sites. The high-density structure of bridgmanite is unstable at ambient pressures, where it readily transforms to a low-density glass if heated.

Some materials from the deep Earth, such as diamonds, are delivered to Earth's surface, but most deep-mantle silicates do not survive the journey to the surface. An exception is a sample of ringwoodite, which reached the surface as an inclusion in diamond and provided evidence for substantial amounts of water in the mantel transition zone (7). Nearly all other natural examples of deep-mantle minerals come from the asteroid belt (8). Hypervelocity impacts on meteorite parent bodies cause short pulses

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Deep-mantle minerals in a meteorite. This shockmelt vein in the L chondrite, Roosevelt County 106, consists of quenched chondritic melt (nearly black matrix) with entrained meteorite fragments. The olivine in the fragments has transformed into deep-blue ringwoodite. The image is about 1 mm wide.

of very high pressures and locally high temperatures that melt and transform meteoritic materials into the same high-pressure phases that make up the deep Earth. During shock, the impacted rocks are compressed to pressures of more than 25 GPa. In highly deformed regions, such as sheer bands or collapsed pores, sample temperatures exceed the melting temperatures of the materials (~2500 K at 25 GPa), resulting in shock-melt veins and pockets (9). It is in and adjacent to these melt zones that olivine, pyroxene, and plagioclase get hot enough to transform into their high-density polymorphs.

Shocked meteorites have provided natural examples of deep-mantle minerals (see the second figure) since Binns *et al.* (10) discovered ringwoodite, the spinel-structured polymorph of olivine, in a shocked chondrite and named it after A. E. Ringwood. Many high-pressure minerals have been named after important high-pressure experimentalists. Bridgmanite is thus a very fitting name for the most abundant mineral in the Earth. Continued investigation of shock effects in meteorites and terrestrial rocks will likely provide many more natural examples of minerals from deep within Earth or other planetary bodies. ■

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PSYCHOLOGY

How quickly we forget

Why do we recall some things better than others?

By David C. Rubin

ince the beginning of the scientific study of human memory, there has been a tension between those who stress experimental control, even at the risk of oversimplifying and thus losing aspects of the behavior of interest (1), and those who stress studying behavior as close as possible to the way it exists naturally, with only enough control to produce replicable results (2, 3). The first approach optimistically assumes that the theory tested in the laboratory will generalize to more varied situations; the second counters that a careful, preferably quantitative, description of the phenomenon is neededclose to its full complexity-before a reasonable theory can be formulated, otherwise important aspects may be removed before a theory is considered. When it is possible, as in the study by Roediger and DeSoto (4) on page 1106 of this issue, combining both approaches is the most productive strategy.

Roediger and DeSoto examined the pattern and rate at which individuals (in the United States) forget U.S. presidents over time. The authors examined two groupsthree generations of students (totaling 415 individuals in 1974, 1991, and 2009) from different U.S. universities, and 497 adults in 2014. Among their observations is a similar pattern of enhanced recall of the first U.S. presidents (Washington, Adams, and Jefferson), of Lincoln, of the current president (at the time of testing), and of presidents close in time to the time of the test (attributed to the "recency effect"). On the basis of their results, Roediger and DeSoto extrapolate when the fame of recent presidents, as measured by the ability of people to recall them, will reach the level of Presidents Fillmore, Buchanan, and McKinley (who were not well remembered).

The findings of the study overall suggest an integration of personal memory and the memory of major historical events. This is because of an observed continuity in memory for historical events (U.S. presidents) that occurred before and after one's birth. The recall data of Roediger and DeSoto decrease smoothly with time from the pres-

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the 1970s), people in the United States forget U.S. presidents in the same way, with strongest recall only for the earliest and most recent presidents (but also for Lincoln) (4).