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Hot Idea —— posted November 28, 2003

Hafnium, Tungsten, and the Differentiation of the Moon and Mars

--- Experiments help us understand the timing of core formation and nature of initial melting in the Moon and Mars.

Multi-anvil module
(Kevin Righter)

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Measurements of the isotopic composition of tungsten (W) show that lunar samples and Martian meteorites have an excess of tungsten-182. This was produced by the decay of hafnium-182 (Hf-182), an isotope with a half-life of only 9 million years. Because tungsten dissolves enthusiastically in metallic iron and hafnium does not, it is possible to use the abundance of W-182 in rocks formed by melting of the silicate mantle as an indicator of the timing of core formation. However, the concentrations of Hf and W in rocky material can be affected by melting and crystallization, so we also need to know how each element concentrates in common minerals in the mantles of the Moon and Mars. The behavior of Hf has been studied experimentally, but this is not true of W. Kevin Righter (Johnson Space Center) and Charles (Chip) Shearer (University of New Mexico) have filled this knowledge void by determining how W partitions between olivine, high- and low-calcium pyroxene, plagioclase feldspar, and garnet.

The new data allowed Righter and Shearer to reexamine available measurements of the isotopic composition of W in lunar samples and Martian meteorites. Their analysis suggests that the lunar magma ocean, a huge magma system that surrounded the Moon when it formed, solidified in less than 30 million years. This is shorter than many theoretical calculations suggest. Pathfinder data and chemical data from Martian meteorites suggest that the core of Mars makes up about 20% of the planet. Core formation and subsequent melting of a region of the mantle containing garnet and high-calcium pyroxene took place less than 20-30 million years after the formation of the first solids in the solar system. This type of research shows the importance of measurements of isotopic compositions of radioactive elements or their decay products and laboratory experiments on the geochemical behavior of those elements.

References:

> Righter, K. and Shearer, C. K. (2003) Magmatic fractionation of Hf and W: Constraints on the timing of core formation and differentiation in the Moon and Mars. *Geochimica et Cosmochimica Acta,* v. 67, p. 2497-2507.
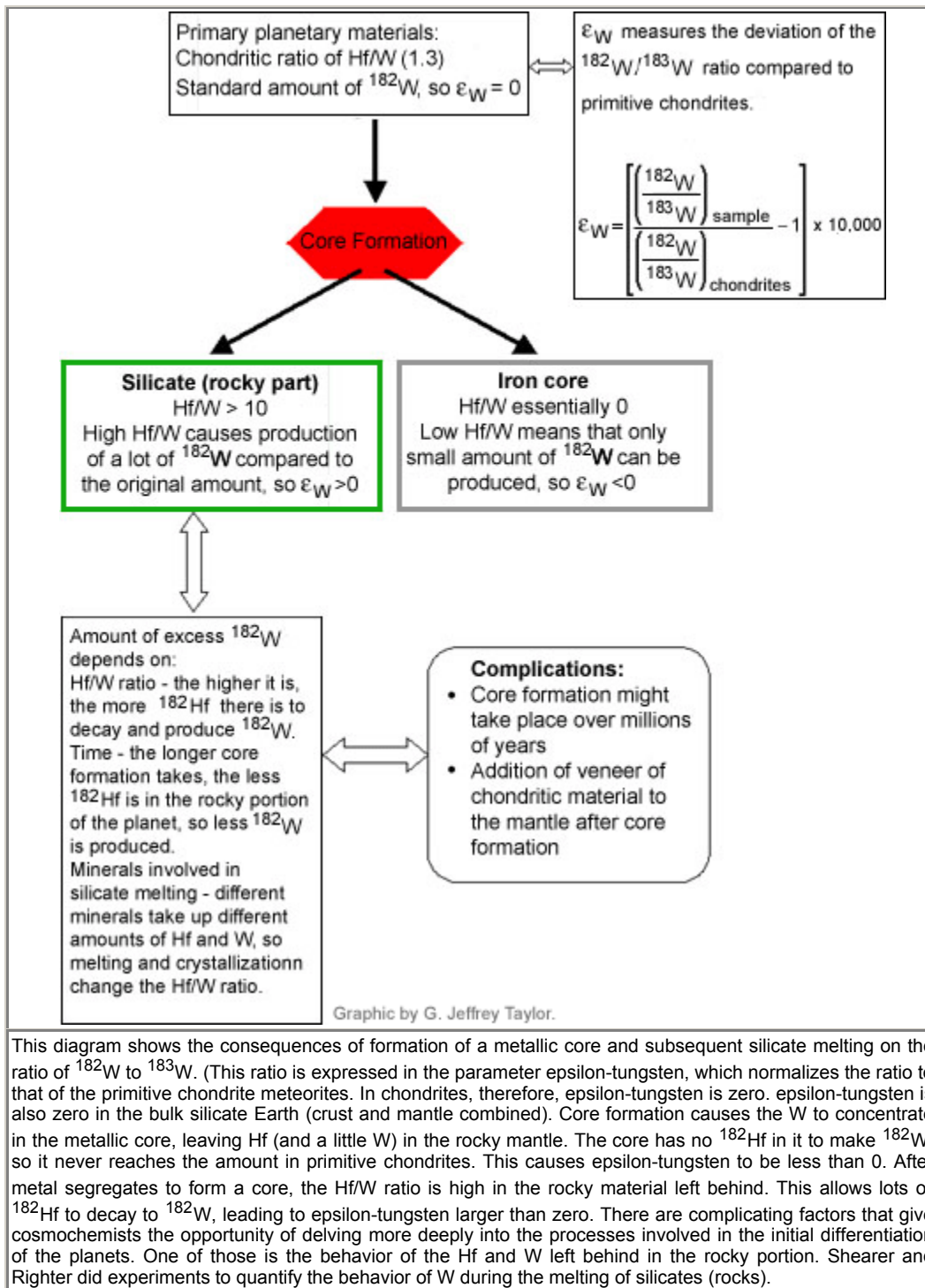
> Shearer, C. K. and Righter, K. (2003) Behavior of tungsten and hafnium in silicates: A crystal chemical basis for understanding the early evolution of the terrestrial planets. *Geophysical Research Letters,* v. 30, doi: 10.1029/2002GL015523.

Short-lived Isotopes and Core Formation

Cosmochemists routinely use numerous isotopic systems to determine the ages of solar system materials. The isotopes include both those with long half lives, such as rubidium-87 ([87]Rb, half life of 48.8 billion years), which decays to strontium-87 ([87]Sr), and those that have half lives that are so short that the radioactive isotope no longer exists. The hafnium-182 ([182]Hf)-tungsten-182 ([182]W) pair is one of those. [182]Hf has a half life on only 9 million years. This means that essentially all of it decayed to [182]W in about six half lives, only 55 million years. While this might seem like a long time, it happened 4.5 billion years ago. The decay of a short-lived isotope gives us a way of precisely dating events that happened long ago. Cosmochemists can determine age differences of only a million years in rocks billions of years old.
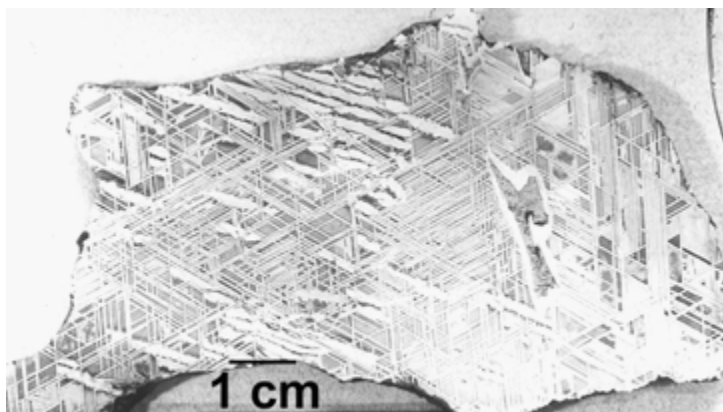
What we are dating depends on the elements involved. In some cases we date the time a solid formed in the solar nebula, the cloud of gas and dust surrounding the nascent Sun. Others might date the time a lava flow erupted onto a planet's surface. Still others can date the time the mantle of a planet first melted. The Hf-W system dates the time metal segregated from rocky materials to form a core and provides a quantitative look at the nature of silicate melting in the newly-formed mantle. The diagram below summarizes the way Hf and W behave as a planet melts early in its history.

This diagram shows the consequences of formation of a metallic core and subsequent silicate melting on the ratio of ^{182}W to ^{183}W. (This ratio is expressed in the parameter epsilon-tungsten, which normalizes the ratio to that of the primitive chondrite meteorites. In chondrites, therefore, epsilon-tungsten is zero. epsilon-tungsten is also zero in the bulk silicate Earth (crust and mantle combined). Core formation causes the W to concentrate in the metallic core, leaving Hf (and a little W) in the rocky mantle. The core has no ^{182}Hf in it to make ^{182}W, so it never reaches the amount in primitive chondrites. This causes epsilon-tungsten to be less than 0. After metal segregates to form a core, the Hf/W ratio is high in the rocky material left behind. This allows lots of ^{182}Hf to decay to ^{182}W, leading to epsilon-tungsten larger than zero. There are complicating factors that give cosmochemists the opportunity of delving more deeply into the processes involved in the initial differentiation of the planets. One of those is the behavior of the Hf and W left behind in the rocky portion. Shearer and Righter did experiments to quantify the behavior of W during the melting of silicates (rocks).

Primitive chondrite meteorites and the rocky portion of the Earth form the standard for comparison of the ratio of ^{182}W to ^{183}W. The latter isotope was not formed by the decay of ^{182}Hf and behaves geochemically just like W, so ^{183}W makes a convenient reference. To compare easily, Der-Chuen Lee and Alex Halliday (Institute for Isotope and Mineral Resources in Zurich, Switzerland), pioneers in the analysis of tungsten isotopes, defined a parameter called epsilon-tungsten, or ε$_w$. This simply compares the ratio of ^{182}W to ^{183}W in a sample to the ratio in the bulk silicate Earth multiplied by 10,000. This is expressed mathematically by the equation shown in the diagram above.

If the tungsten in a chondrite remains in chemical equilibrium, the ^{182}W/^{183}W will remain chondritic because of tungsten exchange among minerals, so epsilon-tungsten will be zero. However, the situation changes dramatically if metallic melting removes iron to form a dense, metallic core. The tungsten concentrates in the metal, leaving behind a metal-free rock that now has a higher Hf/W ratio. The metal would have virtually no Hf, so no additional ^{182}W would be produced. This leads to a low value of ^{182}W/^{183}W in the metallic core. In turn, this causes epsilon-tungsten to be less than zero. Iron meteorites, which formed in the cores of asteroids that melted, have epsilon-tungsten less than zero.

Iron meteorites like the one shown here formed when chondrites melted. The metal, because it was denser than the surrounding silicates, sank to form the core of a tiny planet in the asteroid belt. Because the hafnium stayed behind, there was no source of ^{182}W, giving a value of epsilon-tungsten less than 0.

Edmonton (Kentucky) Meteorite
(Courtesy of Smithsonian Institution.)

The silicate left behind after metal sank to form a core in an asteroid or planet would still have some ^{182}Hf, unless core formation took so long (more than about six ^{182}Hf half lives, or 55 million years) than none remained. This radioactive ^{182}Hf would continue to decay, producing ^{182}W. Because of this production and the high amount of Hf compared to W, the ratio of ^{182}W to ^{183}W becomes larger than chondrites have, so epsilon-tungsten is greater than 0. How much greater depends on several factors such as when the core formed and the resulting Hf/W ratio. The Hf/W ratio can be affected by further melting in the rocky portion of a planet. The ratio in a magma or in the unmelted residue can vary substantially depending on what minerals are present. Cosmochemists, particularly Gordon McKay (Johnson Space Center), have done experiments to map out the way hafnium behaves during melting, but few experiments have been done to understand how tungsten behaves. Shearer and Righter decided to remedy this knowledge gap.


Measuring Element Behavior

Laboratory experiments to determine the geochemical behavior of elements have helped us understand a great deal about the geochemical evolution of the planets. Trace elements are particularly useful because they behave in predictable ways, once some experimental data are available. Cosmochemists can calculate the way elements separate from each other. In the case of radioactive elements, cosmochemists can even date the time when the elements separated.

Kevin Righter took the lead in doing experiments on how tungsten partitions into magma and different minerals as the rock inside a planet melts. The expected minerals to be involved in melting inside planets are olivine, low-calcium pyroxene, high-calcium pyroxene, plagioclase feldspar, and garnet. The idea is to concoct a synthetic rock of the right composition, then heat it until it is partially melted. To be applicable to the interiors of planets, the experiments must be done at elevated pressure. Righter used pressures ranging from 1 bar (atmospheric pressure at the surface of the Earth) to 100 kilobars (a kilobar is 1000 times the atmospheric pressure). Temperatures ranged from 1150 Celsius to 1850 Celsius. Part of the reason for doing the experiments at a range of pressures is that some minerals, such as garnet, form only at high pressure. The high-pressure apparatus, called a multi-anvil, uses octahedral devices that are squeezed between tungsten carbide cubes. (The tungsten carbide is used because of its strength, not because Righter and Shearer were studying the behavior of tungsten. It does not interfere with the experiments on the behavior of tungsten inside the ceramic octahedral.) Some experiments at the low end of the pressure range were done with another type of pressure apparatus called a piston-cylinder device.

(Courtesy of Kevin Righter.)
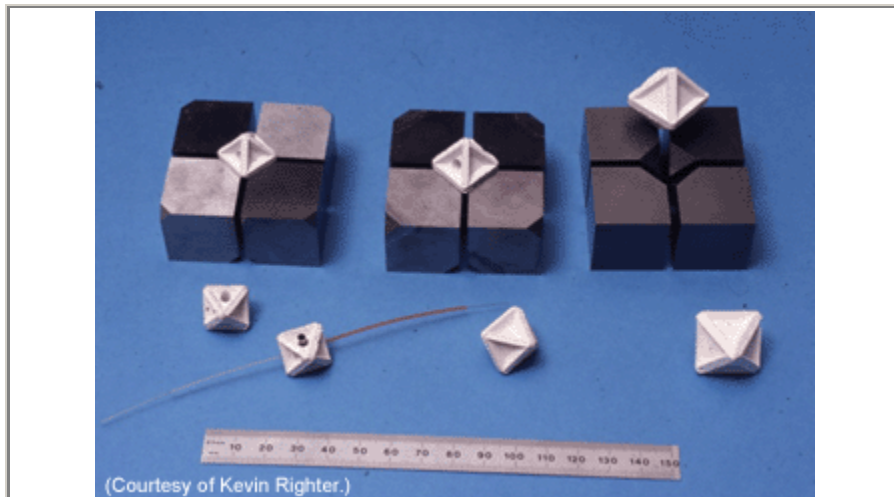
To determine the behavior of tungsten at high temperature and pressure, Kevin Righter used high-pressure apparatus at the University of Arizona. The samples to be studied were placed in the center of ceramic octahedral (white) and then squeezed between eight truncated tungsten carbide cubes (grayish, metallic). (The tungsten does not interfere with the experiments on the behavior of tungsten inside the ceramic octahedral.) Depending on the sizes of the octahedrons and the truncations on the tungsten carbide cubes, pressures between 3 and 30 billion pascals (30,000 to 300,000 times atmospheric pressure) can be obtained. This corresponds to depths of ~100 to 1000 km on Earth and 300 to 3000 km on Mars.

(Courtesy of Kevin Righter.)
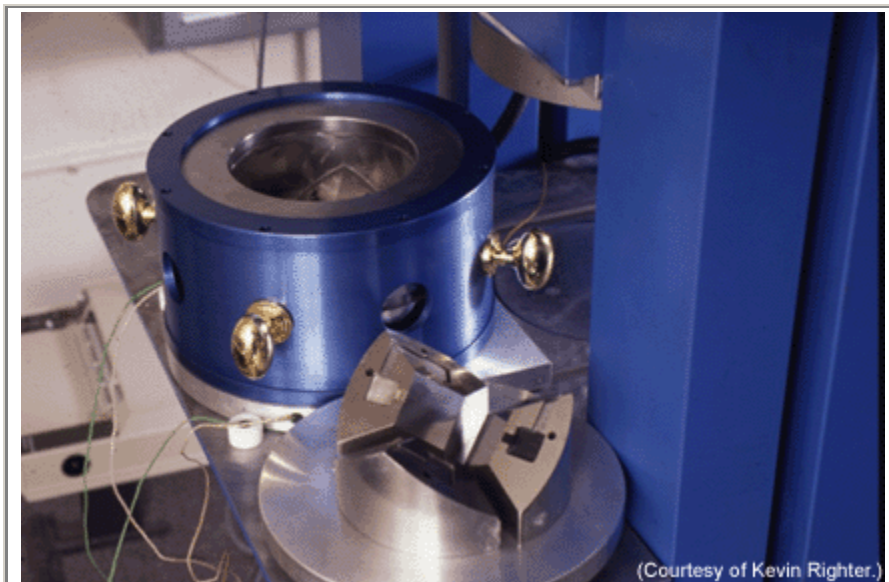
The assembled stack of eight cubes and the sample octahedron is placed in the center of this cylindrical module, between six wedges that are connected to a hydraulic system. The blue module is called a "multi-anvil module."

(Courtesy of Dolores Hill, University of Arizona.)
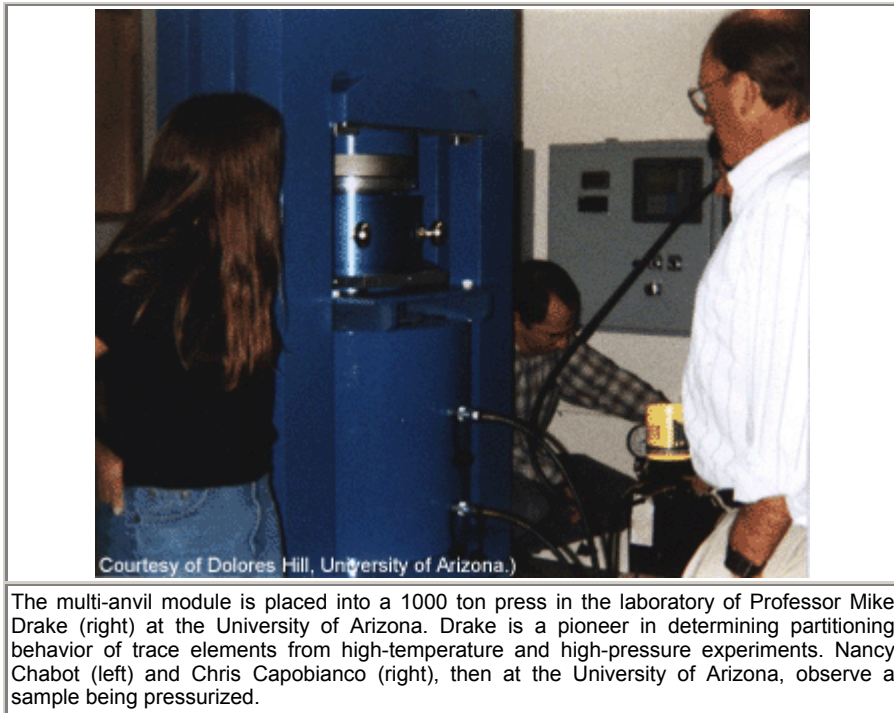
The multi-anvil module is placed into a 1000 ton press in the laboratory of Professor Mike Drake (right) at the University of Arizona. Drake is a pioneer in determining partitioning behavior of trace elements from high-temperature and high-pressure experiments. Nancy Chabot (left) and Chris Capobianco (right), then at the University of Arizona, observe a sample being pressurized.

Righter and Shearer used a range of starting compositions so they could be sure of getting all the minerals of interest to crystallize and to study how the tungsten partitioning varies with mineral composition. They also added about 0.5 wt% WO_3 (and in some cases HfO_2) to be sure there would be enough in all minerals and the magma to measure accurately. To ensure that conditions were not oxidizing (appropriate for planetary interiors), Righter encapsulated the samples in graphite-lined platinum tubing. The graphite forces the system to maintain oxidizing conditions at the right level. It also prevents or at least minimizes loss of iron from the sample to the platinum capsules. (Iron loss would change the chemical properties of the minerals being studied.)

Righter and Shearer measured the chemical compositions of the experimental products on an electron microprobe, a standard device that does chemical analyses on tiny spots (only 1 micrometer across). Chip Shearer measured the tungsten abundances using the ion microprobe at the University of New Mexico. Ion microprobes are very complicated instruments used to measure both isotopes and trace elements. Shearer had to work out assorted interferences from other elements and create a set of standards. Ion microprobe analyses are rarely routine!

The concentrations of tungsten were measured with the ion microprobe at the University of New Mexico. This complicated instrument consists of an ion source, mass spectrometer, and associated electronics and vacuum system. Shown operating the ion probe is Justin Hagerty, a graduate student at UNM.

The partitioning behavior is described by a parameter called the partition coefficient. This is simply the ratio of the concentration of an element in a mineral crystal divided by its concentration in the magma in which the mineral is forming. A partitioning coefficient of 1.0 indicates that the element would have the same concentration in the mineral as in the magma. Partition coefficients less than 1 shows that the element prefers to remain in the magma; those greater than 1 indicate that the element concentrates in crystals in preference to magma. The partition coefficients for tungsten and hafnium determined by Righter, Shearer, and others appear in the table below.

Mineral	Distribution Coefficient for W	Distribution Coefficient for Hf
Olivine	0.02 to 0.07	0.07
Low-Ca pyroxene	0.007 to 0.025	0.08
High-Ca pyroxene	0.04 to 0.19	0.28 to 0.56
Plagioclase	0.003 to 0.03	--
Garnet	0.007 to 0.028	0.20 to 0.52

All the distribution coefficients for tungsten are very low, showing that tungsten concentrates in magma. (However, if metallic iron is present, the tungsten readily concentrates in it.) Distribution coefficients for hafnium are low for olivine and low-Ca pyroxene. This means that those minerals will not cause drastic separation of tungsten from hafnium. This is far from true for high-calcium pyroxene and garnet, however. Tungsten avoids them, but hafnium, though still preferring a magma, concentrates relatively easily into those minerals. This means that when a rocky body melts after metal has segregated to a core, the presence of high-calcium pyroxene and garnet will lower the Hf/W ratio in the magma and increase it in the unmelted part of the rock. Assuming this happens when ^{182}Hf is still present, it will lead to lower epsilon-tungsten in the magma and higher epsilon-tungsten in the solids. This allows cosmochemists to figure out the depth and timing of melting early in a planet's history.


Making Sense of Tungsten Isotopes

Righter and Shearer applied their data to published isotopic measurements of lunar basalts and Martian meteorites. The lunar samples contain excesses of ^{182}W; epsilon-tungsten ranges from 1 to about 4.5. To interpret the data, they calculated what the epsilon-tungsten value would be if core formation happened 30, 40 and 50 million years after the formation of the chondrites. They also calculated the effect of different amounts of fractionation of hafnium from tungsten (expressed in the figure below by different Hf/W). High Hf/W

could have resulted from accumulation of high-calcium pyroxene (cpx in the graph below) and ilmenite (iron-titanium oxide). Lunar scientists believe that high-titanium lunar basalts formed from mantle rocks that formed by accumulated of high-calcium pyroxene and ilmenite in the lunar magma ocean. This would explain the high epsilon-tungsten value one of them has. Low-titanium basalts formed from mantle rocks that accumulate olivine and low-calcium pyroxene, leading to low Hf/W, and low epsilon-tungsten. In both cases, the calculations fit the data best if the core formed no later than 30 million years after the formation of the solar system. This means that materials in the solar nebula accreted into larger and larger objects, forming the Earth and other planets, and then the Moon (probably by a giant impact onto the Earth). As the Moon assembled in Earth orbit, it melted, forming the magma ocean. The magma ocean cooled and crystallized, forming a feldspar-rich crust and dense cumulates that later remelted to form the basalts that make up the maria. And all that happened in 30 million years or less!

(From Righter and Shearer, 2003, Geochemica et Cosmochemica Acta, v. 67, p. 2497-2507.)
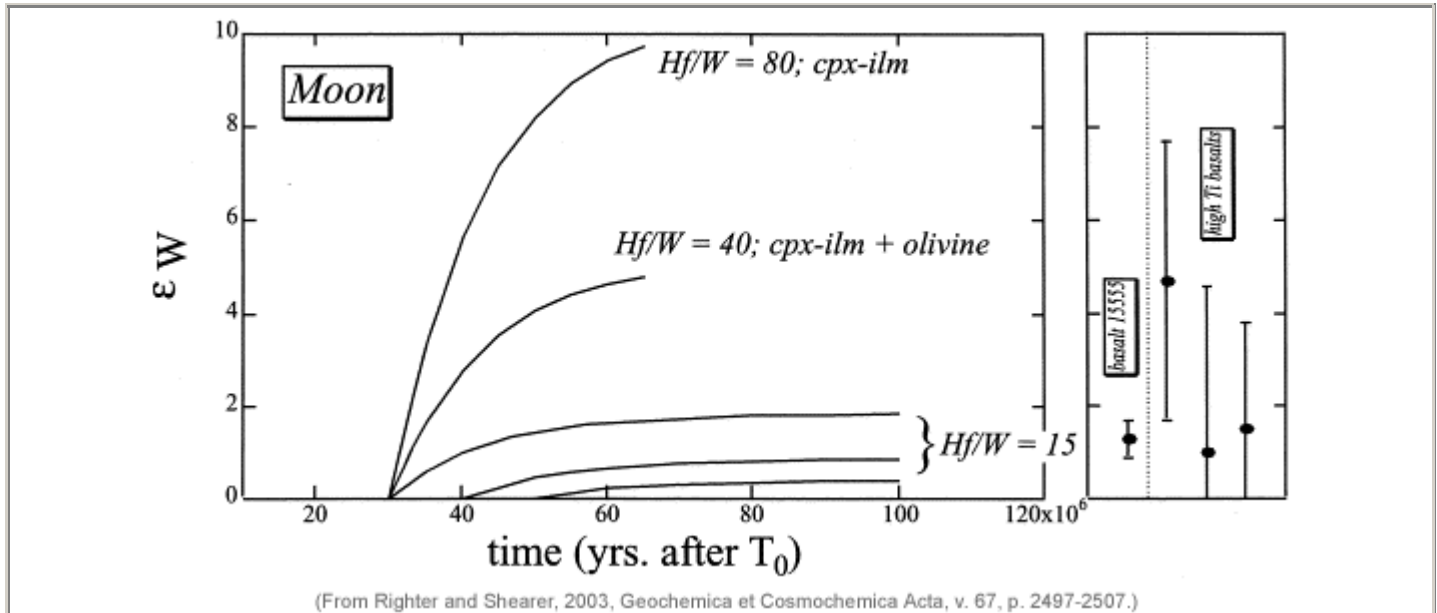
The left side of this diagram shows how epsilon-tungsten would vary with time in the Moon, depending on when the core of the moon-forming impactor formed and on the Hf/W ratio after formation. Because Hf concentrates preferentially over W in ilmenite (ilm) and high-calcium pyroxene (cpx), rocks rich in those minerals will have high Hf/W. Such rocks could form late during the solidification of the lunar magma ocean. When rocks rich in ilmenite and high-calcium pyroxene melted, the magma would also have high epsilon-tungsten. Parts of the Moon that contained only olivine and low-calcium pyroxene would have lower Hf/W and lower epsilon-tungsten. The right side of the diagram shows epsilon-tungsten values for four lunar mare basalts. The data suggest that the magma ocean had to have solidified within 30 million years of the formation of the first solids in the solar nebula. Otherwise, epsilon-tungsten in low-titanium basalts such as 15555 would be lower. Formation of the high-titanium basalts seems to have involved mantle rocks rich in ilmenite and high-calcium pyroxene.

Martian meteorites also have positive values of epsilon-tungsten (see graph below). Righter and Shearer again calculated how epsilon-tungsten would change with time depending on when the core formed and the Hf/W in the mantle. In contrast to the smaller Moon, Mars probably has garnet in it (see cross section of Martian interior). Since garnet is one of the minerals that might greatly affect the ratio of Hf/W, hence the value of epsilon-tungsten, Righter and Shearer looked at several cases. A deep part of the mantle rich in garnet would have very large epsilon-tungsten, exceeding 20. The Martian meteorites do not have values anywhere near that. This does not mean that a mantle like did not form on Mars, only that the Martian meteorites did not form from that type of mantle rock. An alternative is that the small excess of [182]W (small positive epsilon-tungsten) is inherited from a shallow mantle source that contained high-calcium pyroxene and perhaps garnet. For example, a mantle containing consisting of 10% high-calcium pyroxene and 10% garnet (with the remainder being olivine and orthopyroxene) would have a Hf/W of 17. Such a mantle could produce epsilon-tungsten values close to those in Martian meteorites (shown on the right). They also calculate that a garnet-free mantle could have Hf/W of about 7 and would also be consistent with the epsilon-tungsten measured for Martian meteorites. Whatever the details, it appears that the Martian mantle and core could have formed rapidly, easily within 20-30 million years of the beginning of the formation of the solar system.

(From Righter and Shearer, 2003, Geochemica et Cosmochemica Acta, v. 67, p. 2497-2507.)
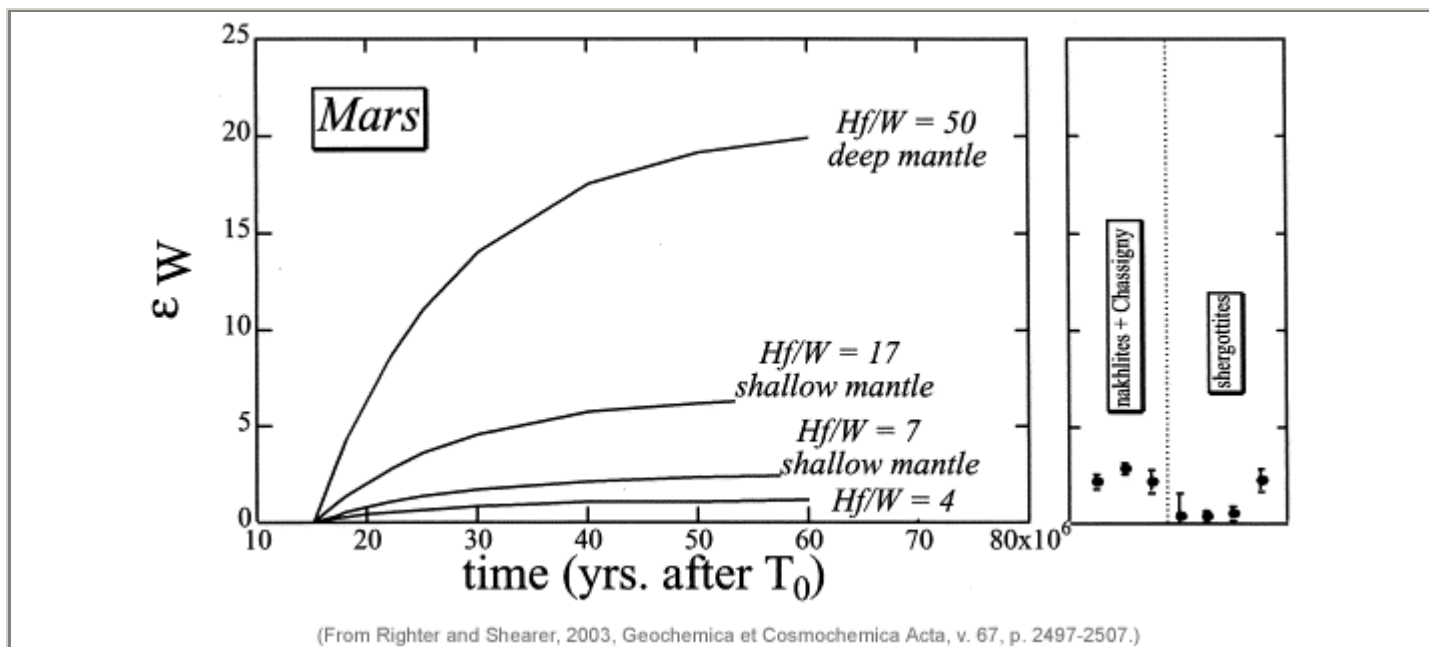
The left side of this diagram shows how epsilon-tungsten would vary with time in Mars, assuming core formation at 15 million years after the beginning of the solar system. The calculated curves are for different Hf/W ratios in the mantle, depending on mineralogy (see diagram below). Because Hf concentrates preferentially over W in garnet, a deep mantle rich in garnet would have high Hf/W. The resulting epsilon-tungsten values would be much larger than in Martian meteorites (right side of diagram). Smaller values like those in Martian meteorites can be obtained if the meteorites come from shallow parts of the mantle that contain less garnet (Hf/W of 7 to 17). Even with the low Hf/W of 7, epsilon-tungsten values like those in the meteorites are obtained within 20-30 million years of the origin of the solar system.

The interior of Mars

(Illustration by Brooks Bays, PSRD graphics artist.)
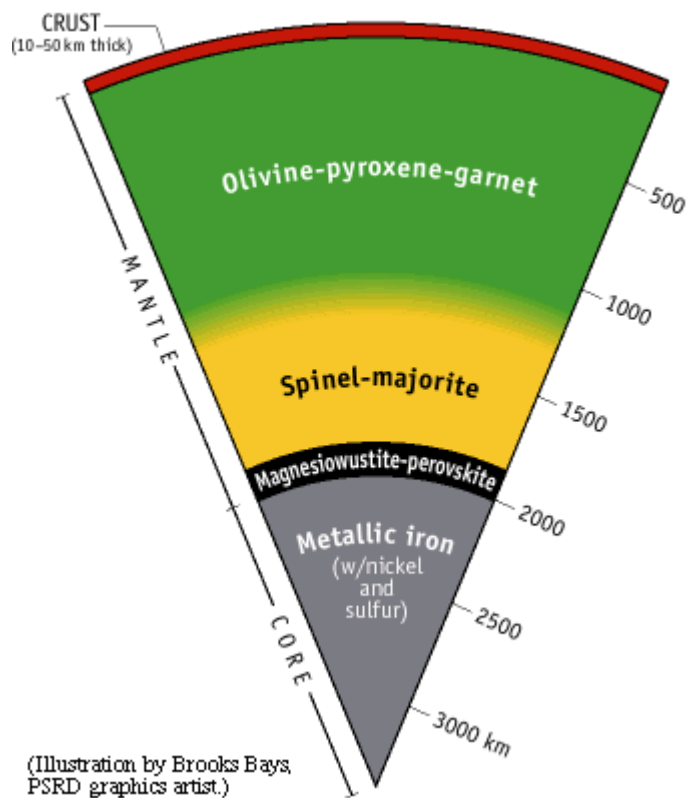
Experiments by Constance M. Bertka and Yingwei Fei (Geophysical Laboratory of the Carnegie Institution of Washington) give us one possible picture of the interior of Mars. In this picture, the uppermost mantle of Mars consists of olivine and pyroxene, with a small amount of garnet (shaded green). However, at a depth of about 1100 km, the olivine begins to convert to a more dense form, called gamma-spinel, without changing its chemical composition. The conversion is complete by 1300 km. Along with the conversion of olivine to a spinel crystal structure, garnet and pyroxene convert to a mineral called majorite, which has a crystal structure like garnet, but is close to pyroxene in chemical composition (shaded yellow). At higher pressures, hence deeper, there is a relatively abrupt transition at 1850 km (shaded black) to a mixture of perovskite (itself a mixture chemically of $MgSiO_3$ and $FeSiO_3$) and magnesiowustite (a mixture of FeO and MgO). The metallic core (shaded gray) begins at about 2000 km depth and continues to the center at a depth of 3390 km. Magma produced by melting in any of the silicate regions above the metallic core will result in different ratios of Hf to W because the two elements partition differently into different minerals.

The Knowledge Matrix

The study of extinct isotopic signatures like the Hf-W system used by Righter and Shearer required several important advances and tools. One is the development of instrumental techniques to measure small differences in the isotopic composition of tungsten. The second is development of high-pressure experimental apparatus. The third is the development of the ion microprobe for trace element analyses of tiny grains. Then these techniques had to be used to measure the isotopic compositions in lunar samples and meteorites, and to determine the geochemical behavior of hafnium and tungsten. Once all that was done, cosmochemists (in this case Kevin Righter and Chip Shearer) synthesized the data into a new understanding of the timing and processes involved as the planets formed and began to evolve geologically. Most cosmochemical research involves such interdisciplinary advances in instrumentation, data, and understanding.

Additional Resources

Halliday, Alex N. (2000) Hf-W chronometry and inner solar system accretion rates. *Space Science Reviews,* v. 92, p. 355-370.

Righter, K. and Shearer, C. K. (2003) Magmatic fractionation of Hf and W: Constraints on the timing of core formation and differentiation in the Moon and Mars. *Geochimica et Cosmochimica Acta,* v. 67, p. 2497-2507.

Shearer, C. K. and Righter, K. (2003) Behavior of tungsten and hafnium in silicates: A crystal chemical basis for understanding the early evolution of the terrestrial planets. *Geophysical Research Letters,* v. 30, doi: 10.1029/2002GL015523.

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