

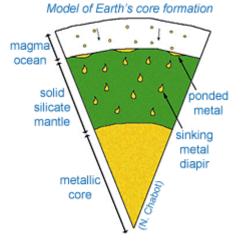
about PSRD archive search subscribe glossary comments

Hot Idea

posted July 7, 2005

Squeezing and Heating Rock to Scope Out How Metallic Iron Dribbled to the Center of the Earth

--- Experiments showing how cobalt and nickel concentrate in molten metal shed light on the formation of Earth's metallic core.



Written by G. Jeffrey Taylor

Hawai'i Institute of Geophysics and Planetology

Formation of Earth's metallic <u>core</u> was one of the most important events in the history of the planet. Metallic iron is much denser than rock, so it sank to the middle, taking other elements that concentrate in metal rather than silicate (rock) with it. However, we do not understand everything about core formation. One particularly niggling puzzle is why cobalt (Co) and nickel (Ni) have the same concentration (relative to primitive carbonaceous <u>chondrites</u>) as one another in Earth's mantle. At low pressure these elements concentrate in metallic iron to different extents. Calculations show that if metal segregated from silicate at low pressure, nickel ought to be 100 times less abundant (normalized to chondrites) than cobalt, not equal.

Cosmochemists have tackled this problem by doing experiments at high pressure and temperature to map out how cobalt and nickel partitioning between metal and silicate differs compared to low pressure. However, the studies differ in their predictions of the behavior because of differences in the assumed pressure, temperature, and oxidation state during core formation. Nancy Chabot (Case Western Reserve University, now at the Johns Hopkins Applied Physics Laboratory), and David Draper and Carl Agee from the University of New Mexico addressed the discrepancies by designing a series of experiments over a wide range in temperature. Their results plot out the conditions under which metal can sink to the core while leading to the observed cobalt and nickel concentrations in the mantle. While the results do not lead to a unique solution, they point the way for further studies of other elements that tend to concentrate in metallic iron, and they show clearly that the equal nickel and cobalt concentrations in the mantle can be the product of core formation in the early Earth.

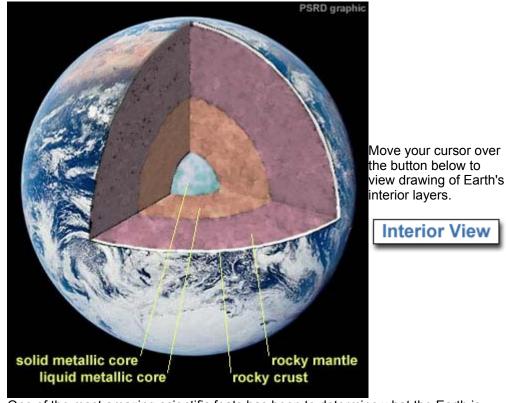
Reference:

• Chabot, Nancy L., David S. Draper, and Carl B. Agee (2005) Conditions of core formation in the Earth: Constraints from nickel and cobalt partitioning. *Geochimica et Cosmochimica Acta*, v. 69, p. 2141-2151.

Journey to the Center of the Earth

A giant steel ball sits at the center of the Earth. The ball reaches about half way to the surface, thereby occupying an eighth of the Earth's volume. The metallic ball, called the core, is surrounded by a rocky shell

called the mantle. Because iron is much denser than rock, the core makes up about 30% of the total mass of the Earth. We know all that mostly from knowing the density of the planet, which indicates that there must be something denser than rock inside, and from its moment of inertia, which says that the mass is not distributed uniformly--the deep interior is denser than shallower parts. The idea that the dense sphere could be made of iron was inspired by finding iron meteorites and figuring that they could be the cores of <u>asteroids</u>. Studies of earthquakes determine the size of the core quite precisely and show that there is an inner solid metallic core.



One of the most amazing scientific feats has been to determine what the Earth is made of inside. Geophysical data establish that a large sphere of metallic iron occupies the deep interior of the Earth. Its center has solidified, but is still hot. It is surrounded by a swirling mass of molten metallic iron and other metals. Motions in that liquid outer core produce Earth's magnetic field. The core is surrounded by a rocky layer called the mantle. The mantle is hot, but solid almost everywhere except in places near the top where low pressure permits it to melt partially. The topmost layer is the crust, which we live on. It is thinner than the picture shows. An intriguing problem in planetary science is figuring out how the core formed.

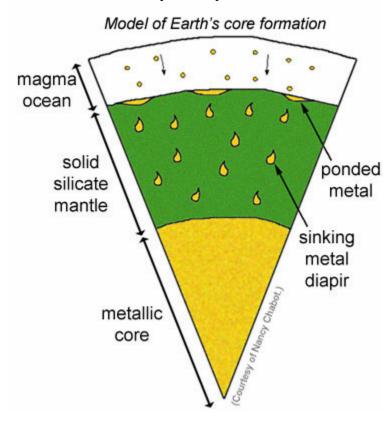
Draining Metal to Middle Earth

How did the metallic iron get to the middle of the Earth? The answer would seem obvious: iron is dense, hence heavy, so it should sink. But it has to sink through rock, which even when hot is strong enough to support fairly hefty masses of iron, and the iron has to migrate to form large, sinkable pods. The simplest way to separate iron is to melt the Earth, or at least a large portion of it. The metallic iron would also melt and fall as droplets to form a core. This implies a hot origin for the Earth.

A hot infant Earth was out of vogue for decades. Many geophysicists thought that it formed cold from cold dust and then heated up slowly as decay of radioactive elements like potassium, uranium, and thorium dumped heat into the mantle. The core was thought to have formed up to a billion years after formation of the planet. Two things changed that view. One was the discovery that when the Moon formed it was surrounded by a huge magma system, hundreds of kilometers deep (see **PSRD** article: Moonbeams and Elements). The other is that

measurements of short-lived isotopes such as tungsten-182 show that the metallic cores of the Earth, Moon, and Mars must have formed within 50 million years of the formation of the oldest materials in the solar system (see PSRD article: <u>Hafnium, Tungsten, and the Differentiation of the Moon and Mars</u>). Since core formation requires a high temperature, the isotope data show that it happened very early in the planet's history.

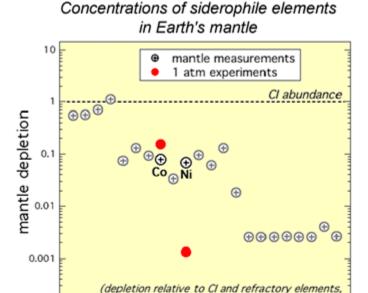
Existence of the lunar magma ocean inspired cosmochemists to devise models depicting a largely molten Earth, including a significant magma ocean (see graphic below). The models use the tendency of some elements to concentrate in metallic iron rather than in silicate magma. Elements that concentrate in iron are called siderophile, which means "iron loving." Siderophile elements have different degrees of affection for iron, which provides cosmochemists with a way to decipher the conditions of core formation.



In this model of Earth's core formation, metallic iron sinks in the partially molten Earth that is surrounded by a magma ocean. The chief uncertainty is in the thickness of the magma ocean, which affects both its pressure and temperature. Other factors also add to the uncertainty in calculating the behavior of elements during core formation, such as its oxidation state and composition of the molten silicate and concentration of other elements in metallic iron.

The concentrations of cobalt (Co) and nickel (Ni) in the mantle provide an important constraint on the details of core formation. Analyses of samples from the Earth's mantle show that siderophile elements are depleted compared to their abundances in chondritic meteorites (see diagram below). The higher the tendency of an element to concentrate in metallic iron, the more depleted it is. Cobalt and nickel are depleted by the same amount. The depletion of these elements is proof of core formation. If no metallic iron had been in contact with molten silicates, they would plot drastically differently on the diagram.

0.0001



Mn V Cr Ga P Fe W Co Ag Ni Sb As Ge Mo Os Re Ir Ru Pt Rh Au Pd

increasing siderophile behavior ->

plotted along the bottom in order of increasing tendency to concentrate in metallic iron. The concentrations represent the concentration in the mantle divided by the concentration in carbonaceous chondrites, which are thought to approximate the relative element abundances of the initial material from which the planets formed. Plotting close to the CI line (equal to 1) indicates little difference compared to carbonaceous chondrites. Most elements plot below the line, indicating that they are depleted in the mantle. Co and Ni are depleted to the same extent, but calculations (red dots on the graph) using their behavior at low pressure predict that Ni ought to be depleted 100 times as much as Co. This has led cosmochemists to investigate the chemical behavior of Co and Ni at high pressures.

Elements in this graph are

The depletion of Co and Ni to the same extent is at odds with predictions from experiments at low pressure (one atmosphere, the same as the surface of the Earth). Element behavior is characterized by use of partition coefficients (D), the concentration of an element in metallic iron divided by its concentration in co-existing molten silicate. The low-pressure partition coefficients for Co and Ni have been measured previously. The surprise is that the partition coefficient for Ni is 100 times higher than for Co. This implies that Ni should be depleted 100 times as much as Co.

volatility corrected)

(Courtesy of Nancy Chabot.)

This discrepancy led cosmochemists to think up explanations for the nickel excess. Some of these ideas are listed below (from a very useful list in Alex Halliday's chapter about the Earth in volume 1 of the **Treatise on Geochemistry**):

Equilibration between metal and silicate at high pressure--elements behave differently at high pressure, so perhaps Co and Ni partitioning will be different.

Equilibration between iron metal enriched in sulfur--partitioning also depends on the compositions of the metal and silicate, and on the temperature. If the metal contained more sulfur than the metal used in experiments, it might accept less Ni. Also, it would be liquid at a lower temperature (adding sulfur depresses the melting temperature), and temperature is another important factor that affects element partitioning.

Inefficient core formation--leaving behind some of the metallic iron-nickel in the mantle would raise the levels of all the siderophile elements.

Heterogeneous accretion of the Earth, leading to the addition of what has been called the "late veneer." The term is misleading, as the idea did not depict addition of a thin coating of metal-bearing silicates being added to the growing Earth. It is really late addition to the upper mantle of material rich in siderophile elements.

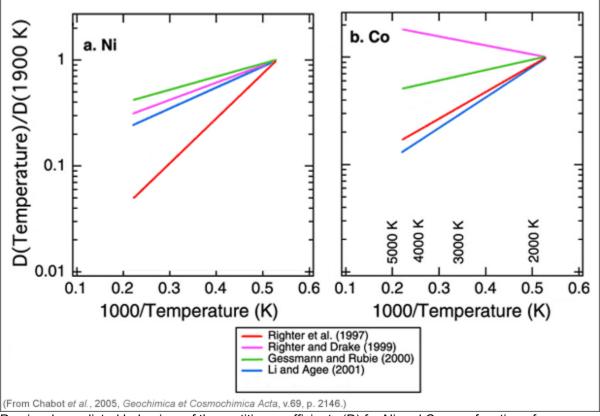
Addition of material to the Earth during the moon-forming event involving impact of a giant projectile--this is the widely accepted (though not proven) idea that a Mars-sized impactor hit the Earth during its growth, forming the Moon from debris flung into orbit (see **PSRD** article: Origin of the Earth and Moon).

Equilibration at extremely high temperature--as noted, element behavior changes as temperature changes.

High-temperature equilibration in a magma ocean at the boundary between what was to become the lower and upper mantle.

It is the last idea that has received the most attention recently and is the focus of the measurements made by Nancy Chabot and her colleagues. Cosmochemists have made such measurements before, but not at the full range of conditions possible in a magma ocean surrounding the infant Earth. For example, pressures predicted in a magma ocean have ranged from 24 to 59 <u>GPa</u> and temperatures have ranged from 2200 to more than 4000 K (4500 to 7700 °F). Also, results of the predictions did not agree with each other (see graphs below), leading to differences for the depth and temperature calculated for the hypothetical magma ocean.

http://www.psrd.hawaii.edu/July05/cobalt_and_nickel.html



Previously predicted behaviors of the partition coefficients (D) for Ni and Co as a function of temperature are drastically different because of differences in the predicted effects of temperature during core formation. The vertical axis is the ratio of the partition coefficient at a given temperature to the partition coefficient at 1900 K. (Partition coefficient in this case means the concentration of Co or Ni in metallic iron divided by the concentration in molten silicate (rock).) The comparison to the D at 1900 K helps show the variation of D with temperature. Temperature is plotted as 1/T (times 1000) because many temperature-dependent parameters vary linearly when plotted versus 1/T rather than T directly.

It is important to obtain a better quantitative handle on core formation. Here's one reason why: Kevin Righter (Johnson Space Center) and Michael Drake (University of Arizona) used measurements of Ni and Co partitioning between metal and silicate to calculate the pressure and temperature conditions in a terrestrial magma ocean that would give the correct depletion factors for Co and Ni. However, the temperature they needed to make the concentrations work out right was lower than the melting temperature of mantle rock at high pressure. This led them to conclude that the magma ocean contained water, which would lower the melting temperature. The presence of water has enormous implications for how and when the Earth received the water that ended up in the oceans--but are the temperature estimates correct? Nancy Chabot realized that more experiments were needed, especially to understand the effect of temperature on partition coefficients.

Experiments Plumb the Depths of the Magma Ocean

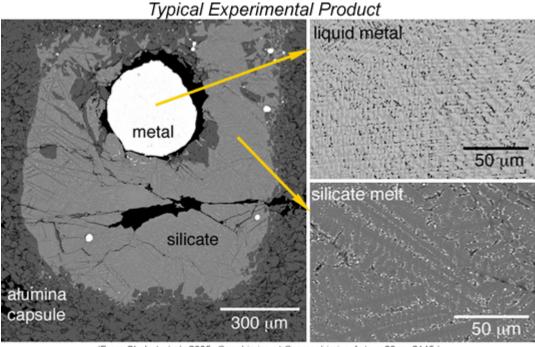
Inside the Earth or in a magma ocean surrounding the Earth as it was forming, the temperature is high and pressures are crushing. To simulate those conditions, cosmochemists use special high-pressure equipment. Chabot and her colleagues used a large device to squeeze a multi-anvil to high pressure (see photograph below). The device was located at the Johnson Space Center and then moved to the University of New Mexico, where co-authors Dave Draper and Carl Agee now work. The samples are placed into a small octahedral sample holder made of a ceramic material. The samples are surrounded by aluminum oxide capsules and sleeves and by rhenium metal, which can be heated to high temperatures. The entire sample is placed inside a huge press and

the pressure increased to the desired level. For this set of experiments, Chabot used 7 GPa (70,000 times atmospheric pressure).



The samples were a mixture of basalt and metal powders. Basalt is a type of lava and is different from the composition of the terrestrial magma ocean, but it allowed the investigators to run experiments at a wide range of temperatures. Such a wide range is not possible with rocks that represent the composition of the Earth's mantle because of their high melting temperature. The important thing in these experiments is the presence of molten silicate and molten metal. The metallic powders consisted of iron with 4 wt% Co and 10 wt% Ni mixed in, and variable amounts of carbon. The amount of carbon varied from none to about 6%. It was added to test the effect of carbon on the Co and Ni partition coefficients. It also lowers the melting temperature of the metal, raising the range of temperatures where the metallic phase remains liquid.

The products of the experiments were blobs of metallic Fe-Ni-C embedded in fine-grained silicates (see figures below). The metal assembled into spherical blobs that when cooled rapidly at the end of each experiment crystallized into branching crystals of metallic Fe-Ni-Co surrounded by spots of carbon-rich metal. The silicate consisted of long crystals of garnet surrounded by tiny crystals of other minerals (not identified) and glass. Ordinarily, a basalt like the one used would crystallize pyroxene and plagioclase feldspar, but at the high pressure and with the aluminum oxide capsules in these experiments, garnet formed instead. Both metal and silicate were analyzed using an electron microprobe.



(From Chabot et al., 2005, Geochimica et Cosmochimica Acta, v.69, p. 2145.)

In the experimental products, blobs of metallic iron containing nickel and carbon formed in the molten silicate. These back scattered electron images were taken with an electron microprobe. When cooled rapidly at the end of an experiment, the metal formed crystals of carbon-free Fe-Ni (white in the top right photograph) surrounded by dark areas of carbon-rich metal. Silicate cooling produces garnet (dark in bottom right photograph) surrounded by other silicate minerals, oxides, and glass. The metal and silicates were analyzed with an electron microprobe using a defocused beam 20 to 50 micrometers in diameter. Electron microprobes focus a beam of electrons on a sample. The electrons produce X-rays from elements in the sample. The X-rays are characteristic of each element and the number of X-rays (counted with a special detector) is proportional to the amount present.

Cobalt and Nickel Behavior Quantified

Five factors might affect the way Co and Ni partition into metal and silicates: (1) the oxidation state of the metal and silicate system, (2) the composition of the silicate, (3) pressure, (4) the composition of the metallic liquid, and (5) temperature. Previous experiments have shown how the first three factors affect Co and Ni partitioning; the experiments by Chabot and her colleagues address the effects of metallic composition and temperature. Each factor is discussed briefly below.

Oxidation state of magma is expressed as the oxygen fugacity, which is a measure of the amount of oxygen available for reaction. Although oxygen makes up about half of almost every rock, the amount that is not already bound to other elements is the oxygen fugacity. It is as if there is a tenuous oxygen atmosphere present. The oxygen fugacity is usually expressed as the variation with respect to some mineral assemblage. For example, if quartz (SiO_2), fayalite (Fe_2SiO_4), and magnetite (Fe_3O_4) are all present, they will keep the oxygen fugacity constant. They buffer it. Chabot estimated the oxygen fugacity compared to the iron-wustite buffer (Fe metal and FeO) by measuring the concentrations of iron in metal and iron oxide in silicates. Previous results have shown that values of the logarithms of the Co and Ni partition coefficients are proportional to -0.5 times ΔIW , where ΔIW is the oxygen fugacity relative to the fugacity at the iron-wustite buffer. The lower the oxygen fugacity, the lower the ΔIW value. Because of the logarithmic dependence, a value of -1 is a factor of ten below the iron-wustite buffer; a value of -3 is 1000 times lower.

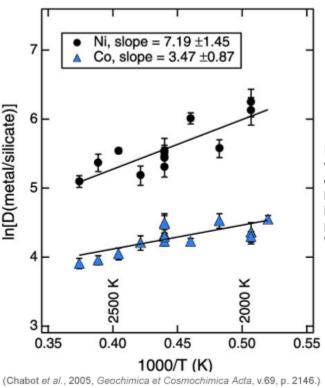
Silicate composition does not make much difference in the case of Co and Ni. Both are divalent (doubly

charged ions) in rocky melts over a wide range of oxygen fugacity.

Pressure makes a big difference. Six previous experimental studies determined that with increasing pressure, Co and Ni both partition less strongly into the metallic melt, but the effect of pressure is more pronounced for Ni than for Co.

The new experiments by Chabot and colleagues show that the composition of the metallic liquid does not make any significant difference in the way Co and Ni partition between metal and silicate. The experiments were done with a range of carbon concentrations and Chabot found no significant differences in partitioning as a function of carbon content. That factor can be safely ignored. Sulfur can have an effect on the partitioning of Co and Ni, but at sulfur concentrations relevant to core formation in the Earth (<10 wt%), that factor can also be safely disregarded.

The variation of Co and Ni partitioning with temperature is where the experiments done by Chabot and co-authors greatly expand our understanding of the terrestrial magma ocean. The great variety of predicted behaviors of Co and Ni described above were due in part to too small a range of temperatures used in previous experiments. The Chabot experiments fill in the big gaps. The experiments show that Co and Ni behavior changes with temperature. The partition coefficients for each decrease with increasing temperature, but the change with temperature is greater for Ni (see graph below).



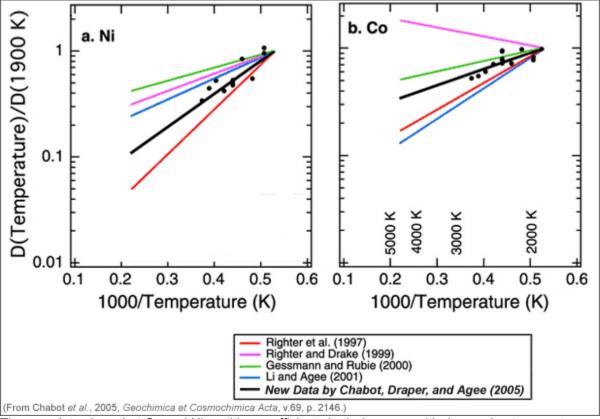
Partition coefficients for Ni and Co vary with temperature. Partition coefficients are plotted on a logarithmic scale (using the natural logarithm) and temperature is plotted as the inverse temperature times 1000.

Using the Measurements

Once the experiments were complete, Chabot and her teammates wanted to use the new and previous data to understand conditions in a terrestrial magma ocean. The hard part of doing that is that the partition coefficients of Co and Ni vary with temperature, pressure, and oxygen fugacity, all at once. They solved this problem by using all available data to devise an equation that captures the variation with temperature, pressure, and oxygen fugacity. Others have created such equations previously and used them to model core formation, but they did not have the benefit of knowing the full range of variation with temperature. The Chabot equation does not

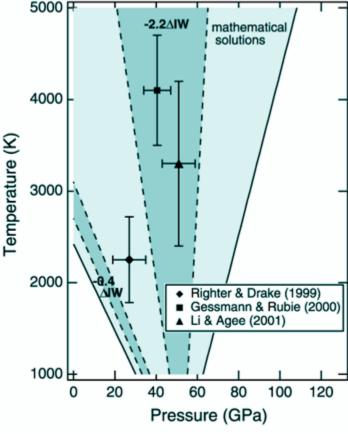
include the effects of silicate or metal compositions, which Chabot shows are not significant. (Other elements in the metal besides carbon and sulfur, such as silicon, hydrogen, and oxygen, might affect the partitioning of Co and Ni. More experiments are needed to test how significant those effects would be.)

The parameterized equation allowed Chabot and associates to compare their results to those obtained by others. In the graphs below (shown earlier but without the new data) partition coefficients for Ni and Co are shown relative to their value at 1900 K (thus they all plot at 1 there) for a pressure of 7 GPa and 1.5 log units below the IW buffer. The new data plot inside the range given by previous reports, but show that the prediction of increasing Co partition coefficient with increasing temperature is not consistent with the new results.



The new data show that Co and Ni partition coefficients both decrease with decreasing temperature, and fall between most previous estimates.

The parameterized equation also allowed Chabot to calculate what conditions could lead to an equal amount of partitioning of Co and Ni. The down side is that there is not one unique solution. Instead, plotting temperature against pressure leads to a large field of acceptable solutions. The acceptable solution set includes all of those suggested by previous research (see graph below). More importantly, the conditions show that Co and Ni abundances in the Earth's mantle can be matched by core formation at high pressure and temperature and low oxygen fugacity, an idea previously rejected by Righter and Drake on the basis of available experimental data. Righter and Drake instead suggested that lower temperatures were required, which drove them to infer that water was present in the mantle. (Water lowers the melting temperature of magma.) Chabot's new results do not disprove the wet magma ocean idea, but show that other possibilities are in the running.



(From Chabot et al., 2005, Geochimica et Cosmochimica Acta, v.69, p. 2149.)

Lightly shaded area represents all solutions that result in Co and Ni being depleted to the same extent in the Earth's mantle. The darker blue wedges show solutions at the indicated oxidation conditions; they are consistent with results from other studies. The calculations show that a low temperature, water-bearing magma ocean is not required to produced the observed Co and Ni concentrations in the mantle, but do not rule it out.

An Unfinished Job

Like most questions in cosmochemistry, this one is far from answered. There are many complications that the experiments do not take into account. A major one is that the metal and silicate may equilibrate over a range of pressures as metal dribbled to the core, not just one pressure. Future calculations need to take that into account. In addition, there are other siderophile elements whose behavior under a range of conditions needs to be determined. Those elements, especially those cosmochemists call moderately siderophile, might help us narrow down the range of possible conditions in the terrestrial magma ocean.

Studies like these also relate to measurements of the time for core formation using the concentrations of tungsten isotopes, models of the formation of the Earth and Moon, and investigation of cases where the silicate is only slightly molten. It is a fascinating, interdisciplinary problem whose solution will lead to an improved understanding of a major event in the history of our planet.

11 of 1

Additional Resources

LINKS OPEN IN A NEW WINDOW.

- Chabot, Nancy L., David S. Draper, and Carl B. Agee (2005) Conditions of core formation in the Earth: Constraints from nickel and cobalt partitioning. *Geochimica et Cosmochimica Acta*, v. 69, p. 2141-2151.
- Gessmann, C. K. and D. C. Rubie (2000) The origin of the depletions of V, Cr and Mn in the mantles of the Earth and Moon. *Earth Planet. Sci. Lett.*, v. 184, p. 95-107.
- Halliday, Alex N. (2004) The origin and earliest history of the Earth, Chapter 20 in Treatise on Geochemisry, v. 1. (A. M. Davis, editor), p. 510-557.
- Li, J. and C. B. Agee (2001) The effect of pressure, temperature, oxygen fugacity and composition on partitioning of nickel and cobalt between liquid Fe-Ni-S alloy and liquid silicate: Implications for the Earth's core formation. *Geochim. Cosmochim. Acta*, v. 65, p.1821-1832.
- Righter, K., M. J. Drake, and G. Yaxley (1997) Prediction of siderophile element metal/silicate partition coefficients to 20 GPa and 2800 □ C: the effects of pressure, temperature, oxygen fugacity and silicate and metallic melt compositions. *Phys. Earth Planet. Int.*, v. 100, p. 115-134.
- Righter, K. and M. J. Drake (1999) Effect of water on metal-silicate partitioning of siderophile elements: a high pressure and temperature terrestrial magma ocean and core formation. *Earth Planet. Sci. Lett.*, v. 171, p. 383-399.
- Taylor, G. J. (1997) Moonbeams and Elements, *Planetary Science Research Discoveries*. http://www.psrd.hawaii.edu/Oct97/MoonFeO.html.
- Taylor, G. J. (1998) Origin of the Earth and Moon, *Planetary Science Research Discoveries*. http://www.psrd.hawaii.edu/Dec98/OriginEarthMoon.html.
- Taylor, G. J. (2003) Hafnium, Tungsten, and the Differentiation of the Moon and Mars, *Planetary Science Research Discoveries*. http://www.psrd.hawaii.edu/Nov03/Hf-W.html.



[About PSRD | Archive | Search | Subscribe]

[Glossary | General Resources | Comments | Top of page]

psrd@higp.hawaii.edu

main URL is http://www.psrd.hawaii.edu/