For now, it remains unproven which hypothesis—"balance" or "naproxen"—accounts for the increased thrombotic events associated with rofecoxib treatment. As Cheng and colleagues point out, these two hypotheses are in fact mutually compatible. Large-scale clinical trials of these compounds need to be instigated with patients suffering from cardiovascular disease. Because of continuing concerns, Merck will enroll about 30,000 subjects in trials to resolve questions about the cardiovascular safety of both rofecoxib and the newly announced selective COX-2 inhibitor, Arcoxia (etoricoxib) (*12*). Perhaps an academic group, such as the Oxford-based Antithrombotic Trialists' Group (*13*), will take an interest in resolving the present imbalance between perception and evidence of a cardiovascular hazard from selective inhibitors of COX-2.

References and Notes

1. S. Bunting, S. Moncada, J. R. Vane, *Br. Med. Bull.* **39**, 271 (1983).
2. Y. Cheng *et al., Science* **296**, 539 (2002).
3. G. A. FitzGerald *et al., N. Engl. J. Med.* **310**, 1065 (1984).
4. B. F. McAdam *et al., Proc. Natl. Acad. Sci. U.S.A.* **96**, 272 (1999).
5. F. Catella-Lawson *et al., J. Pharmacol. Exp. Ther.* **289**, 735 (1999).
6. S. S. Jick, *Pharmacotherapy* **20**, 741 (2000).
7. C. Bombardier *et al., N. Engl. J. Med.* **343**, 1520 (2000).
8. G. A. FitzGerald, C. Patrono, *N. Engl. J. Med* **345**, 433 (2001).
9. A. S. Reicin *et al., Am. J. Cardiol.* **89**, 204 (2002).
10. W. A. Ray *et al., Lancet* **359**, 118 (2002).
11. T. Murata *et al., Nature* **388**, 678 (1997).
12. F-D-C Reports *The Pink Sheet* (17 December 2001).
13. Antithrombotic Trialists' Collaboration, *Br. Med. J.* **324**, 71 (2002).
14. J.R.V has received payment to act as a consultant and/or to speak at conferences in the past 3 years from Boehringer Ingelheim, Merck Inc., Parke-Davis, Rhone-Poulenc Rorer, and Shire Pharmaceuticals.

PERSPECTIVES: GEOLOGY

Osmium Remembers

Richard W. Carlson

On page 516 of this issue, Meibom and Frei (*1*) report isotopic analyses of mineral grains picked from stream deposits in Oregon and California. From these data, they derive conclusions about geochemical processes that occurred long ago in Earth's core. How can minute crystals found in a riverbed provide information on Earth's deep interior?

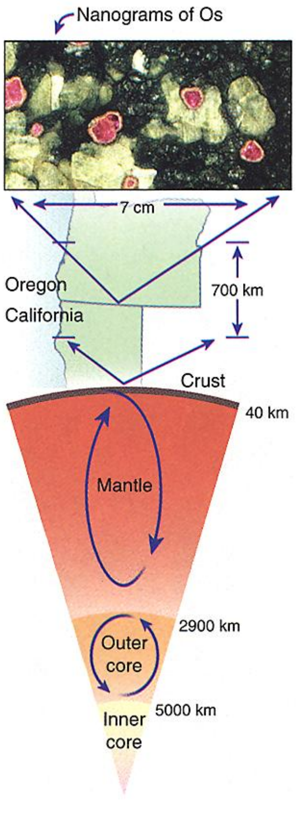
Enhanced online at www.sciencemag.org/cgi/content/full/296/5567/475

Less than 50 years ago, plate tectonic theory delivered the realization that Earth's interior is not rigid but is in continual motion driven by thermal convection. The data reported by Meibom and Frei provide further evidence that convection in Earth's interior has caused at least some portions of the mantle to circulate to its two thermal boundary layers (the crust and the core) not once, but several times over Earth's history. Reading the "core signal" in their samples, the authors suggest that the solid inner core began to form within 250 million years of Earth's formation. This conclusion has far-reaching implications for the history of the magnetic field and the thermal evolution of Earth.

Meibom and Frei examined the isotopic composition of osmium (Os) in rare Os-metal alloy grains, which had been weathered from mantle rocks now exposed in the crust of Oregon and northern California (see the figure). Some of the osmium is formed via the decay of two radioactive elements. The rhenium isotope ^{187}Re (half-life, 41.6 billion years) decays to ^{187}Os, and the platinum isotope ^{190}Pt (half-life, 449 billion years) to ^{186}Os. Osmium is present at only parts per billion levels in the mantle, but it is highly concentrated into mineral phases such as iron-nickel-sulfide and the Os-metal alloys studied by Meibom and Frei. Consequently, these Os-rich minerals are exceedingly rare and well-separated spatially from one another in the mantle.

Because of the separation between these minerals and the strong chemical affinity Os has for them, diffusion is ineffective in mixing Os isotopic composition across any substantial distance in the mantle. In this respect, the osmium system differs from other radiometric systems, such as rubidium-strontium and samarium-neodymium, which have been used for decades to study the melting history of Earth's mantle. These elements are widely distributed throughout the silicate minerals that make up the majority of the mantle. Because of diffusion at high mantle temperatures, the isotopic consequences of small-scale chemical heterogeneity are averaged out in these radiometric systems. The record of discrete events in the chemical differentiation of the mantle is smoothed as a result.

In contrast, the grains studied by Meibom and Frei show a wide range of Os isotopic compositions, which can be translated into formation ages for the individual grains. The resulting ages range from 256 to 2644 million years ago. The rocks from which these minerals were presumably derived were added to North America between 160 and 500 million years ago. The wide range of Os model ages most likely reflects the inability of convective stirring and diffusion to homogenize Os isotopic composition in the mantle. In essence, the Os isotopic system records multiple events in the chemical differentiation history of the mantle.



Connecting sand grains in Oregon to the inner core. Meibom and Frei measured the isotopic composition of osmium extracted from millimeter-sized grains weathered from bodies of mantle rock (7-cm-wide section of rock shown) tens of kilometers in size, accreted to the Oregon-California crust by collision between North America and the oceanic crust of the Pacific. In this collision, most of the oceanic plate sank and became involved in a mantle convection system that reaches from Earth's crust to the core. The chemical history of crystallization of the inner core, recorded in the composition of the outer core, is transferred to the mantle by material exchange across the core-mantle boundary. This "core signal" will be brought back to the surface as mantle convection circulates the lowermost mantle to the surface.

A particularly intriguing aspect of the data presented by Meibom and Frei is that their samples have higher ^{186}Os/^{188}Os ratios but generally lower ^{187}Os/^{188}Os ratios, in comparison to the average mantle. Low ^{187}Os/^{188}Os ratios are a common feature of mantle regions from which partial melts have been extracted (*2*). They result from removal of Re, which preferentially partitions into the melt while Os stays behind in the solid. But because Pt follows Re

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into the melt, melt-depleted mantle should also have low ^{186}Os/^{188}Os, unlike Meibom and Frei's samples.

Elevated ^{186}Os/^{188}Os accompanied by high ^{187}Os/^{188}Os has been reported in lavas from Siberia (*3*) and Hawaii (*4*). Oceanic basalts have been known for some time to have high ^{187}Os/^{188}Os, and this was generally attributed to the presence of recycled crust in the mantle (*2*). (Crust is generated by melting of the mantle and will therefore have high Re/Os and Pt/Os.)

Brandon *et al.* (*4*) argued that the magnitude of variation in ^{186}Os/^{188}Os seen in Hawaiian lavas was too great to explain by mixing old crust back into the mantle. They attributed the result instead to the incorporation of a small amount of core material into the mantle before it departed from the core-mantle boundary and rose as a thermal plume beneath Hawaii. Based on what is known from iron meteorite analogs, crystallization of the inner core will leave the outer core with high Pt/Os and Re/Os. Because Os concentrations in the core are much higher than in the mantle, even a fraction of a percent of core material will noticeably alter the Os isotopic composition of the mantle.

Meibom and Frei's results indicate that, in their samples, core-mantle mixing and the formation of the Os-alloys must have occurred long ago, before the core's ^{187}Os/^{188}Os ratio grew to exceed that of the modern mantle. They further use the data to derive constraints on the partitioning behavior of Re, Pt, and Os during core crystallization and suggest that formation of the inner core must already have been well under way within 250 million years of Earth's formation.

This conclusion is of considerable interest because a solid inner core appears to be critical in establishing a dipole magnetic field by controlling convective circulation in the liquid outer core. Furthermore, early inner core formation implies rapid initial cooling of Earth. Given the present size of the still-liquid outer core, this limits subsequent heat loss from the core over Earth's history (unless the core has its own heat source via incorporation of radioactive elements like uranium and/or potassium, a possibility that is not widely accepted). The amount of heat transfer across the core-mantle boundary influences both the vigor of mantle convection and whether the mantle flow leaving the boundary is characterized by broad upwellings or narrow plumes. Elucidating the transfer of heat and material across the core-mantle boundary is thus of crucial importance for understanding the dynamics—and chemical consequences—of convection in the solid earth.

References

1. A. Meibom, R. Frei, *Science* **296**, 516 (2002).
2. S. B. Shirey, R. J. Walker, *Annu. Rev. Earth Planet. Sci.* **26**, 423 (1998).
3. R. J. Walker *et al.*, *Geochim. Cosmochim. Acta* **61**, 4799 (1997).
4. A. D. Brandon, R. J. Walker, J. W. Morgan, M. D. Norman, H. M. Prichard, *Science* **280**, 1570 (1998).

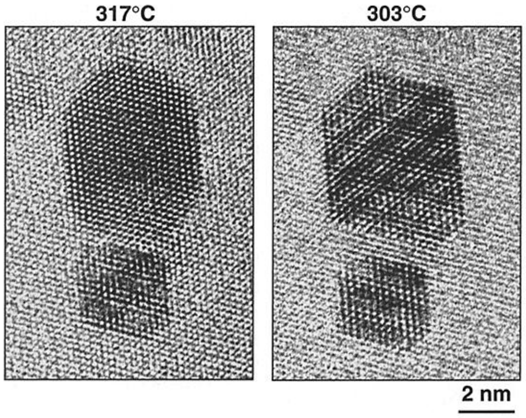
PERSPECTIVES: PHASE OF MATTER

The Elusive Liquid-Solid Interface

Erik Johnson

In macroscopic terms, the boundary between a liquid in contact with a solid surface is described by an interface energy that determines how the liquid wets or spreads out on the surface. If the interface energy is high, wetting is limited; if the interface energy is low, there is nearly complete wetting; in between, one talks about partial wetting. On a microscopic level, the interface is a two-dimensional surface with macroscopic dimensions along the contact surface, yet perpendicular to the surface, it is often considered as a discontinuity with infinitesimal thickness.

During the last couple of decades, however, it has become clear that the structure of the liquid-solid interface is more complex than anticipated. Experiments and computer simulations have shown that a degree of ordering progresses in layers from the solid surface over a few atomic distances into the liquid. On page 507 of this issue, Donnelly *et al.* (*1*) beautifully demonstrate this phenomenon for liquid xenon in contact with aluminum crystal facets. They report high-resolution transmission electron microscopy (TEM) of aluminum samples containing liquid xenon inclusions within faceted aluminum cavities. By viewing the samples with the aluminum facets in an edge-on orientation, they were able to look along the interface and obtain direct evidence for ordering parallel to the interface in the liquid xenon in the three layers nearest to the aluminum surface.



Solidification of a lead inclusion in aluminum. Solidification occurs at a lower temperature than the bulk melting point of 327°C. In the image on the left, taken at 317°C, the larger, somewhat rounded inclusion is still liquid, whereas it has solidified in the image on the right, taken at 303°C, and regained full faceting. The small inclusion is solid in both images. The lattice seen in the liquid inclusion is from the enclosing aluminium matrix, making it impossible to ascertain whether layer ordering exists in the liquid. The images obtained by Donnelly *et al.* (*1*) from xenon inclusions in aluminum are superior because in this particular case, the contrast from the aluminum matrix could be diminished by carefully selecting the orientation of the samples.

The authors used ion implantation to produce aluminum samples containing xenon inclusions a few nanometers in diameter. They exploited the property that a small particle—free or embedded—is confined under a pressure $P = 2\gamma/r$, where r is the radius of the particle and γ is the surface energy for a free particle or the interface energy for an embedded particle (*2*). The interface energy between xenon and aluminum is practically equal to the surface energy of aluminum of 1.2 J m^{-2} (*3*). For inclusions with r < 2 nm, it follows that P is in the Gigapascal range, high enough for xenon to be solid at room temperature. Somewhat larger inclusions will be under lower pressure and contain liquid xenon.

Solid noble gas inclusions in aluminum were first discovered by conventional TEM around 1984 (*4, 5*). Recently, Furuya and co-workers (*6, 7*) have produced beautiful atomic-resolution TEM images of solid xenon inclusions. Similar TEM studies have been carried out on solid lead inclusions embedded in aluminum (*8*). During heating experiments carried out in the TEM, it has been possible to follow the melting and solidification transitions of the lead inclusions in situ (see the figure) (*9*). However, no insights into

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