

What Is in the Earth's Core Besides Iron?

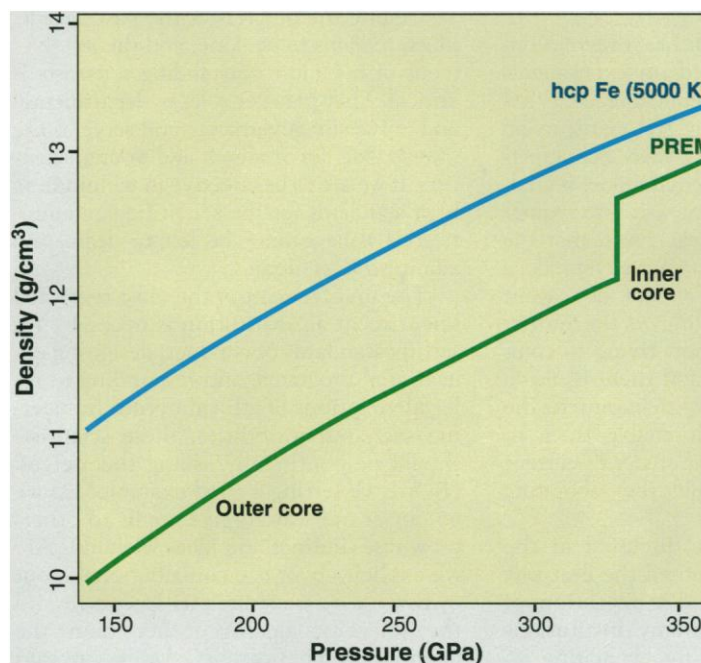
William A. Bassett

There are several questions about the Earth's core that persist. One is why the outer core has a lower density than expected for pure iron; another is what exactly produces the Earth's magnetic field. If it is produced by convection in the molten outer core, what drives the convection? Where does the energy come from?

Studying the Earth's interior is like putting together a giant jigsaw puzzle. As pieces are put in place, a picture of the Earth's inner structure, dynamics, and composition emerges. Most of the pieces have come from seismologists, geochemists, and mineral physicists. Seismologists found that the outer core does not carry transverse (S) waves and is therefore considered to be a fluid. Geochemists studying meteorites observed evidence that iron and nickel phases had once existed in the interiors of planets as molten metal. One of the most recent pieces of the puzzle has been provided by the laboratory study of iron oxide at high pressure and temperature reported on page 1678 of this issue by Fei and Mao (1).

Some of the earliest jigsaw pieces from laboratory studies were put in place by Birch (2-4), the man who is often considered to be the first mineral physicist. He proposed a simple empirical equation that relates sound velocity to the density and mean atomic weight of the material the sound passes through. What is remarkable about this relation, known as Birch's law, is that the velocity of sound can be measured in the Earth's interior as seismic waves travel from an earthquake on one side of the Earth to a seismograph on the other and can also be measured in the laboratory by sending ultrasound through samples at controlled pressures and temperatures. It was Birch who confirmed that the core is composed mostly of iron. At the same time, he made people aware that the outer core has too low a density to be pure iron or iron-nickel alloy. Ever since then, earth scientists have been trying to figure out what element or elements might be responsible for the low density of the outer core. Birch himself considered silicon, sulfur, and oxygen. In later years, hydrogen and carbon were added to the list of light elements under consideration. Poirier, in an

excellent review (5), discusses the discrepancy between the seismically determined density within the Earth's core and the experimentally determined density of iron at the pressures and temperatures that prevail within the core (see the accompanying figure). He then proceeds to consider each of the light elements that have been suggested to explain this discrepancy and evaluates them in light of the criteria that need to be met. There are arguments for and against all of them.



The puzzle piece added by Fei and Mao (1) is important; Fei and Mao's diamond cell, which can achieve both high pressures and high temperatures, allows them to explore parts of the pressure-temperature (P - T) field that were not possible before. When they turned their attention to FeO, what they found is that the high pressure-high temperature phase of FeO that is stable at the P - T conditions of the Earth's core has the nickel arsenide structure (B8 in the Strukturbericht system). The nickel arsenide structure can be thought of very simply as the hexagonal version of the cubic rock salt structure (B1). The rock salt structure describes FeO at ambient P - T conditions. The iron atom is surrounded by six oxygen atoms in both structures, but in the hexagonal structure, the site occupied

by the iron atom is distorted: The Fe-O bonds are allowed by the symmetry to be of different lengths, some shorter than others. Likewise, some Fe-Fe bonds can also be shorter. This means that a very real change in the physical properties is possible. In this atomic arrangement, FeO can behave more like a metal because of the shorter Fe-Fe distances. This discovery may now explain why FeO becomes a good electrical conductor at high P - T conditions, as has been reported by Knittle and Jeanloz (6). Also, the change in properties is consistent with a greater solubility of FeO in molten iron at high pressures, thus helping to explain and support the observations of Ohtani *et al.* (7), Kato and Ringwood (8), and Ringwood and Hibberson (9, 10) that FeO is readily soluble in molten iron at high P - T conditions. This in turn strengthens oxygen as a candidate for an important component of the outer core.

A comparison illustrating the discrepancy between the seismically determined density within the Earth's core [preliminary reference Earth model (PREM)] and the experimentally determined density of iron at core pressures and temperatures [hcp Fe (5000 K)]. The label, hcp Fe (5000 K), stands for the hexagonal close-packed phase of iron believed to exist at core pressures of 140 to 360 gigapascals and temperature of ~5000 K. The difference in density in the outer core is about $10 \pm 2\%$. [Adapted from (1)]

Poirier (5) concludes his review with a statement that it seems inescapable that several light elements are in the outer core and that it is not even obvious that one element should be particularly dominant. He goes on to say that "phase diagrams of iron-rich and iron-nickel-rich ternary and quaternary systems should be experimentally determined up to high pressures and/or calculated." Until these complex systems are better understood, we will not be able to completely understand some of the other questions about the core, such as the mechanism that drives the convection responsible for the Earth's magnetic field. It seems plausible that the convection is driven by the rising of light elements through the molten outer core as those light elements are driven from the solid

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core during solidification. A complete understanding of this, however, will have to wait until we have a better knowledge of those ternary and quaternary diagrams suggested by Poirier. One thing is certain, however, our understanding of these complex questions will depend on observations from many sources. One of the most important of those sources is experiments on the materials present in the core, experiments like the one reported by Fei and Mao. It is the excitement of finding the missing pieces and seeing a picture of some place that is so utterly inaccessible slowly emerge that makes this kind of research so exciting and rewarding.

References

1. Y. Fei and H.-K. Mao, *Science* **266**, 1678 (1994).
2. F. Birch, *J. Geophys. Res.* **57**, 227 (1952).
3. ———, *J. R. Astron. Soc.* **4**, 295 (1961).
4. ———, *J. Geophys. Res.* **69**, 4377 (1964).
5. J. P. Poirier, *Phys. Earth Planet. Inter.* **85**, 319 (1994).
6. E. Knittle and R. Jeanloz, *Geophys. Res. Lett.* **13**, 1541 (1986).
7. E. Ohtani, A. E. Ringwood, W. Hibberson, *Earth Planet. Sci. Lett.* **71**, 94 (1984).
8. T. Kato and A. E. Ringwood, *Phys. Chem. Miner.* **16**, 524 (1989).
9. A. E. Ringwood and W. Hibberson, *ibid.* **17**, 313 (1990).
10. ———, *Earth Planet. Sci. Lett.* **102**, 235 (1991).
11. J. V. Badding, H. K. Mao, R. J. Hemley, in *High Pressure Research: Application to Earth and Planetary Science*, Y. Syono and M. H. Manghnani, Eds. (Terrapub, Tokyo/AGU, Washington, DC, 1992), p. 363.

Binding Site Revealed of Nature's Most Beautiful Cofactor

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The marvelous structure of vitamin B₁₂ was provided by Dorothy Hodgkin and her co-workers in 1956 (1). This accomplishment was the prelude to a very exciting period in cofactor biochemistry in which the first carbon-cobalt bond was identified in the two active cofactor forms of the vitamin (2)—adenosylcobalamin (AdoCbl) and methylcobalamin (CH₃Cbl). The efforts of chemists, biochemists, and spectroscopists converged to elucidate how these important cofactors and their unusual chemistry participate in enzyme-catalyzed transformations and the biosynthetic pathway of B₁₂ (3). In addition, the total synthesis of these amazingly complex and beautiful molecules was achieved (3). The field then remained dormant until the molecular biological revolution renewed enthusiasm for B₁₂. All the genes of B₁₂ biosynthesis have been cloned, sequenced, and expressed, providing an unprecedented—and colorful—view of this pathway and its unanticipated chemistries (4, 5). The crystallization of *Escherichia coli* methionine synthase has now provided the first picture of how methylcobalamin binds to one domain (27 kilodaltons) of this 136-kilodalton (6) protein. The unanticipated and mechanistically thought-provoking structure is presented by Drennan, Huang, Drummond, Matthews, and Ludwig in this issue of *Science* (page 1669) (7).

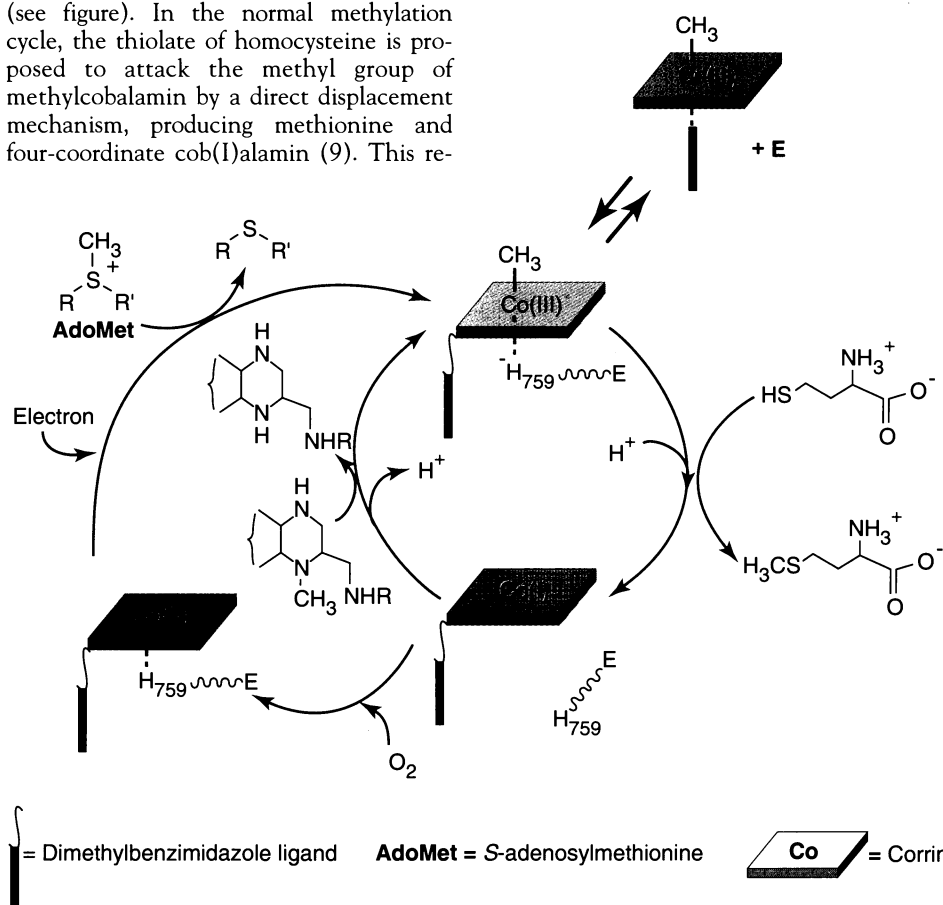
Methionine synthase in *E. coli* (coded by the *metH* gene) and in mammalian sys-

tems is a large, conformationally flexible protein that utilizes all three cofactors with methylating capabilities: N₅-methyltetrahydrofolate (CH₃-THF), methylcobalamin, and S-adenosylmethionine (AdoMet) (8) (see figure). In the normal methylation cycle, the thiolate of homocysteine is proposed to attack the methyl group of methylcobalamin by a direct displacement mechanism, producing methionine and four-coordinate cob(I)alamin (9). This re-

active species then attacks an "activated" form of N₅-methyltetrahydrofolate, again by a direct displacement mechanism, to generate tetrahydrofolate and regenerate methylcobalamin.

The structure of the methylcobalamin domain of methionine synthase has provided unanticipated mechanistic insight into the normal methylation cycle. The dimethylbenzimidazole, providing the sixth ligand of methylcobalamin in solution, is not coordinated to the cobalt on the protein, but is bound instead in a hydrophobic pocket. Furthermore, His⁷⁵⁹ from the protein has now taken its place as an axial cobalt ligand (see figure) (7). The structure also has suggested to the authors a mechanism for how the methylcobalamin might cycle, via a protonation and deprotonation shuttle, between six-coordinate cob(III)alamin and four-coordinate cob(I)alamin (see figure).

A second aspect of the structure is also intriguing. The top face of the corrin, which bears the methyl group to be transferred, is almost completely protected by hydrophobic residues from the helix bundle domain. Homocysteine cannot approach this methyl group, when it is in this protected form, to execute a direct displacement reaction. Given the size of intact methionine synthase and the fact that three



Chemistry performed by methionine synthase.

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