GEOPHYSICS

Changing Views on Earth's Deep Mantle

Robert D. van der Hilst

While spacecraft travel ever farther in space, the rocky world deep below us remains mysterious. Yet, the present-day state and dynamics of Earth's interior hold the keys to understanding the early conditions of the solid Earth and its biosphere, hydrosphere, and atmosphere, and how these have evolved to the planet we now know. Earth's stable stratification into crust (between 5 and 70-km thick), mantle (from base of crust to ~2890-km depth), and core (2890- to 6371-km depth) has been known for half a century from seismic velocity measurements, but characterizing the heterogeneity within and the interaction between these concentric shells is a frontier of modern, cross-disciplinary research. On page 853 in this issue, Trampert *et al.* (*1*) break new ground with compelling evidence for large-scale variations in composition in Earth's mantle.

Man-made probes into the Earth's interior barely reach a depth of ~10 km, and volcanism rarely brings up samples from deeper than ~150 km. These distances are dwarfed by Earth's dimensions, and our knowledge of the deeper realms is pieced together from a range of surface observables, meteorite and solar atmosphere analyses, experimental and theoretical mineral physics and rock mechanics, and computer simulations. A major unresolved issue concerns the scale and nature of mantle convection, the slow (1 to 5 cm/year) stirring that helps cool the planet by transporting radiogenic and primordial heat from Earth's interior to its surface. The mantle displays a velocity discontinuity at 660 km. Does convection occur within separate layers or over the whole mantle? Is the mantle effectively homogenized or has large-scale compositional heterogeneity survived long-term mixing? Classic models have focused either on convective layering (with the upper and lower layers having different, but constant, composi-

tion), or on isochemical whole-mantle overturn, but neither satisfies all multidisciplinary constraints (*2–5*).

Over the past decade, several discoveries have begun to reveal a lower mantle that is far more interesting—and enigmatic—than the bland shell of near-constant properties considered in the classic models. Seismic tomography demonstrates that the 660-km discontinuity is, at least locally, permeable to convective flow (*6, 7*), implying that any chemical stratification must be deeper. Moreover, slabs of subducted tectonic plates that sink into the lower mantle do not appear to all reach the core-mantle

boundary (*8, 9*), which may suggest poor vertical mixing of the mantle (*5*). Mantle plumes remain a topic of debate (*10*), in part because seismological constraints on their nature and size are still ambiguous. But the existence in the deep mantle, for instance beneath Africa, of seismically slow structures with velocity anomalies and gradients too large for a purely thermal origin is uncontroversial (*11*). Seismologists also discovered discrepant behavior of different types of seismic waves, another smoking gun for compositional heterogeneity (*12–14, 15*). In particular, anomalous frequencies of Earth's free-oscillation modes yield a conspicuous anticorrelation between shear speed and mass density, which is inconsistent with a thermal cause (*16*).

Besides providing the data needed to calculate the effect on elastic parameters of changes in temperature, pressure (which is related to depth), and composition, mineral physicists are slowly unraveling the secrets of deep-mantle mineralogy. Recent findings
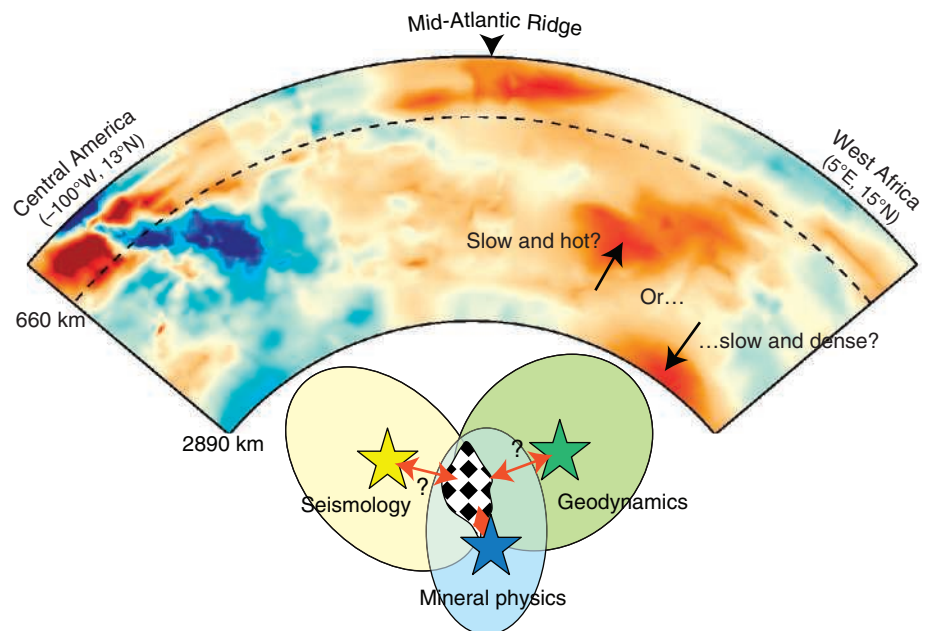
Mantle view in motion. (Top) Primary *(P)*-wave speed variations in the mantle between Central America and Africa, from Earth's surface to the core-mantle boundary (~2890-km depth). The blue structure on the left depicts the slab of subducted lithosphere of the former Farallon tectonic plate, which dips very deep into the mantle, whereas the red structures on the right mark the low wave speeds deep beneath West Africa. Trampert *et al.* (*1*) argue that the traditional view that slow wave speed implies high temperatures (and thus positively buoyant material) is not always correct and that deep in the mantle slow wave speed may be due to higher intrinsic density (negatively buoyant material). The tomographic model (*30*) shown here is constructed from the travel times of different primary wave types (*P, PP, pP, PKP, PP-P,* and *P*diff—the letters denote various geometries of body wave propagation), using finite frequency sensitivity kernels and an irregular grid parameterization. **(Bottom)** Optimal fits to incomplete data sets (stars) are not unique, often strongly influenced by prior assumptions and regularization, and not necessarily accurate. For quantitative data and model integration, common ground (checkered area) must be found by exploring uncertainty. Trampert *et al.* (*1*) perform a full model space search and error analysis.

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include a modified perovskite structure near 88 GPa (~2000-km depth) (*17*); a change from high- to low-spin state of iron between 70 GPa (~1700-km depth) and 120 GPa (~2600-km depth) (*18*, *19*), which may affect rheology (and thus convective mixing) and iron partitioning among magnesiowüstite and perovskite; and a phase transformation to postperovskite near 120 GPa (between 2600- and 2700-km depth) (*20*, *21*).

Meanwhile, geodynamicists have tried to reconcile data from different lines of inquiry with various models for thermochemical convection (*3*, *4*, *22–26*). The postulation that the bottom third of the mantle might be chemically distinct (*9*, *27*, *28*) was a bold departure from existing views and triggered much skepticism and debate. Indeed, absent more definitive observations, the nature, scale lengths, and even the very existence of chemical heterogeneity remained in question. Moreover, quantitative integration of results from monodisciplinary studies was often hampered by inadequate uncertainty analyses.

Trampert *et al*. (*1*) take the quantitative interpretation of red and blue tomographic images (for example, see the figure) to a new level. They hijacked a supercomputer for several months and computed a million model realizations. Using a modern compilation of mineral physics data, with realistic uncertainties, they calculated probability density functions for temperature and composition (parameterized by iron and perovskite variations) from a large set of seismic normal mode and surface wave propagation measurements.

Their wave speed models, which agree with previous results (*15*, *16*), and mineral physics data combine to suggest that compositional heterogeneity is ubiquitous, and is particularly strong beneath 2000-km depth. Assuming a thermal origin, low seismic velocities are often attributed to elevated temperatures. But the new results suggest that such direct scaling is unwarranted because shear speed and temperature are poorly correlated. In addition, at the high pressures of the deep mantle there is little thermal expansion, and so the chemical contribution to buoyancy outweighs the thermal effect. The large, slow "super plume" structures deep beneath the Pacific, Africa, and the South Atlantic appear denser than average, but, perhaps surprisingly, not anomalously hot.

The new quantitative constraints on mantle heterogeneity validate earlier claims (*9*, *16*) and will surely spark questions about Earth's bulk silica composition and thermochemical evolution over geological time. Does the inferred perovskite variation affect the average Mg/Si ratio of the mantle? Can deep perovskite and iron-rich mantle domains be formed and maintained by present-day tectonic processes? Are they leftovers from fractionation in an ancient magma ocean? Are

they fed by chemical interaction between silica mantle and liquid iron core (*29*)? Or—more likely—is a combination required? How do they influence mass and heat flux between deep and shallow mantle and between mantle and core? Are the new seismological observations reported by Trampert *et al*. (*1*) related to the reported changes in mineralogy between 70 and 90 GPa (*17–19*)? For instance, could the strong perovskite-iron correlation in the deep mantle be related to preferential iron partitioning into perovskite owing to a change in spin state?

Finer spatial resolution is needed to determine the spatial length scales of compositional heterogeneity and at what depth the main transitions occur. Furthermore, the conclusions depend on the mineral physics data, which are in flux. The effect of iron on shear modulus is a subject of debate, as are the effects of aluminum (Al_2O_3) and the spin state and oxidation state of iron on bulk mineralogy and elasticity. Indeed, with Al^{3+} and Fe^{3+} largely unaccounted for, new discoveries are surely looming on the horizon. Finally, geodynamicists face the continued challenge of incorporating new constraints from seismology and mineral physics and exploring the implications of the pressure, temperature, and compositional dependence of such key parameters as thermal expansion and thermal conductivity. These are all exciting targets for cross-cutting research in our quest to understand the inner workings and past behavior of our planet.

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BIOCHEMISTRY

How Active Sites Communicate in Thiamine Enzymes

Frank Jordan

It is thought that there is communication between active sites in homodimeric and homotetrameric enzymes (that is, enzymes composed of two or four identical protein chains, respectively). However, identifying the mechanism of communication between these active sites has proved challenging. Traditionally, hypotheses about how enzyme active sites communicate have been based on kinetic evidence (*1*). But access to many more high-resolution structures and greater insight into how conformational dynamics regulate enzyme kinetics provide compelling reasons to re-examine some of these hypotheses. On

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page 872 of this issue, Frank and co-workers (*2*) do just that with their analysis of the bacterial pyruvate dehydrogenase (PDH) complex.

The PDH complex is a thiamine (vitamin B1)–dependent enzyme that shows ping-pong kinetics, that is, it can catalyze two successive half-reactions. The PDH complex converts pyruvic acid (the product of glycolysis) to acetyl–coenzyme A, which then reacts with oxaloacetic acid to produce citric acid at the entry point to the tricarboxylic acid (Krebs) cycle. The first subunit of the PDH complex (E1) carries out a reaction typical of 2-oxo acid decarboxylases using thiamine diphosphate (ThDP) as a cofactor. This E1 subunit exists in three distinct quaternary structures: the "simplest" is an α_2 homodimer, the next is a