

the evolution of both the total energy and the angular momentum as collisional stabilization takes place.

As discussed above, the calculation of the energy-dependent rate constants is computer intensive but proven. The theoretical description of collisional energy transfer has been more elusive. Two components are required: the collision frequency and the magnitude of the changes in E and J , ΔE and ΔJ , occurring upon collision. A theoretical framework has been available for some time—it is recognized that large values of ΔE and ΔJ are less likely than small values—but previous approaches have been empirical. Jasper *et al.* calculated the magnitude and probability distributions of ΔE and ΔJ using large numbers of trajectory calculations, in which methane molecules collide with a third body such as He. The results were used in the master equation calculations, and the final values of the temperature- and pressure-dependent rate constants for $\text{CH}_3 + \text{H}$ were then compared with existing experimental data (6) and showed excellent accord. This is a substantial achievement, in that no fitting of the calculations to experiment was used—the calculations were entirely *ab initio*, and their work provides a means of accurately predicting rate parameters for pressure-dependent reactions.

There is still some way to go before predictions can be routinely made for all pressure-dependent reactions. Some such reactions involve multiple potential energy wells as the initial adduct isomerizes by intramolecular atom transfer. Dissociation from the isomers to several products is often possible, and the rate constants for the different product channels depend in different ways on the total energy and angular momentum. Such reactions are central components of, for example, models to increase the efficiency of automotive engines (7). The extension of the methodology described by Jasper *et al.* to such reactions places considerable demands on the quantitative description of the E - and J -dependent energy transfer processes and on the master equation modeling. Although extension to such reactions is challenging, their work shows that it is achievable. ■

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10.1126/science.aaa1257

GEOLOGY

Driving the Earth machine?

The region of the mantle directly below the tectonic plates plays a key role in mantle flow and volcanism

By Don L. Anderson¹ and Scott D. King²

The asthenosphere—derived from the Greek *asthenēs*, meaning weak—is the uppermost part of Earth's mantle, right below the tectonic plates that make up the solid lithosphere. First proposed by Barrell 100 years ago (1), the asthenosphere has traditionally been viewed as a passive region that decouples the moving tectonic plates from the mantle and provides magmas to the global spreading ridge system. Recent studies suggest that the asthenosphere may play a more active role as the source of the heat and magma responsible for intraplate volcanoes. Furthermore, it may have a major impact on plate tectonics and the pattern of mantle flow.

Earth is a thermodynamic engine powered by its own finite internal reserves of fossil and radiogenic heat that are gradually brought to the surface and radiated to space. Mantle convection cannot be compared with a coffee percolator or a lava lamp, which are systems heated from below by outside energy sources. As Earth cools, the lithosphere cools and sinks (in the form of cold subducting slabs), displacing warmer material in the deeper mantle, which rises as broad passive updrafts. Recent convection simulations show that the region beneath the lithosphere is hotter than expected, and this has rekindled interest in the asthenosphere's role in Earth's engine.

Although comparatively thin, the asthenosphere has a remarkable impact on the mantle. Numerical simulations without an asthenosphere show a pattern of narrow plumes through which material wells up from the bottom of the mantle. When the simulations include a weak asthenosphere, this pattern changes to just two broad upwellings (2). These upwellings are consistent with large low-shear velocity provinces seen at the base of the mantle in global tomography models (see below) (3). Although some researchers have called these upwellings superplumes, we feel that this term is confusing, because fluid dynamicists describe plumes as features driven by their intrinsic buoyancy. Convection simulations with an asthenosphere show that these anomalies instead form in response to plates and subducting slabs (2, 4, 5). Indeed, the asthenosphere may be a necessary component of any

self-consistent model of plate tectonics (6, 7).

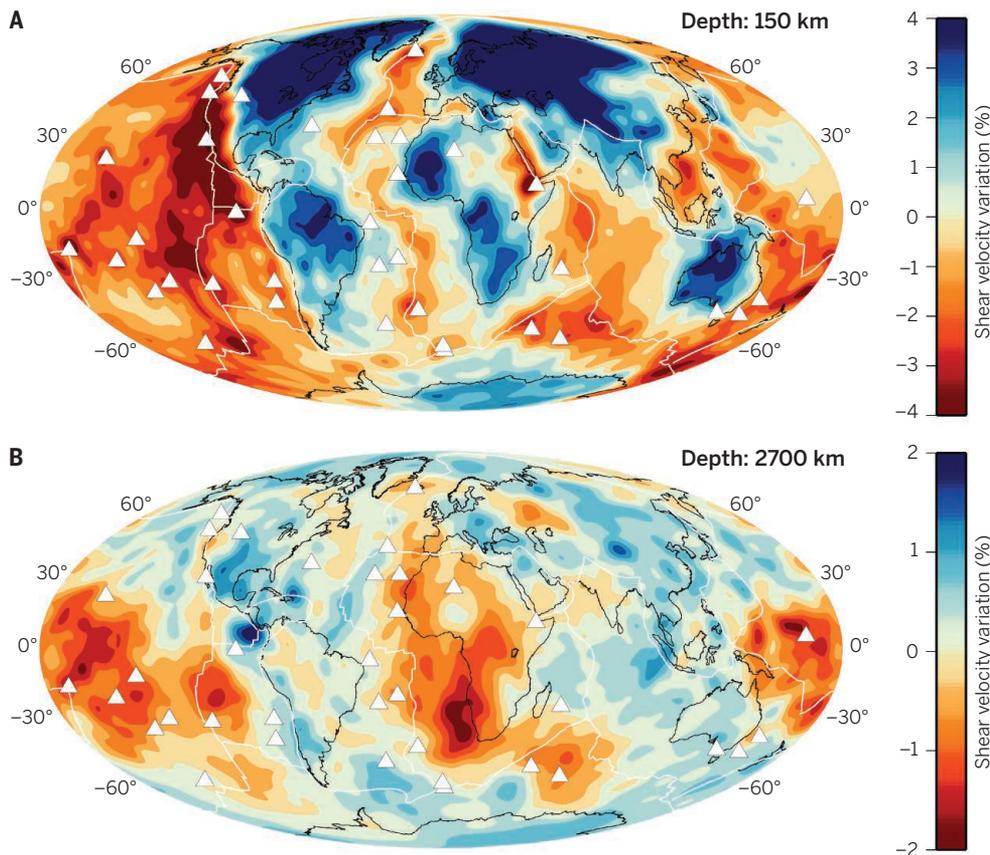
Caught between the mobile lithospheric plate above and the rest of the mantle below, the asthenosphere is a region of concentrated shear. Shearing and the resulting weak coupling between plates and the mantle have a profound influence on the composition of lavas. Near mid-ocean ridges, lavas tend to have homogeneous compositions, whereas lavas that erupt in the middle of tectonic plates are geochemically heterogeneous. The latter have been attributed to

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plumes that upwell from the deeper mantle, with the heterogeneity of the lavas thought to reflect heterogeneity in the mantle plume. However, Samuel and King (8) have shown that these differences may instead arise from differences in the degree of asthenosphere mixing. This mixing is very efficient near the ridge axis, but far from the ridge, the degree of mixing can drop by orders of magnitude. Geochemically heterogeneous lavas may be derived from these poorly mixed domains in the asthenosphere (9), and a plume may be unnecessary.

Geophysical observations have long indicated the existence of a region of low material strength and low seismic velocities beneath the lithosphere, but the depth range of these properties (which define the asthenosphere) and a physical explanation for the seismic and mechanical properties have proven more elusive. These properties are consistent with the presence of partial melt (10). However, some melting experiments did not produce sufficient melt to explain the observations (11). In a remarkable series of experiments, Li and Weidner have shown that a solid with pockets of melt oriented by the shearing can produce the kind

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Top or bottom? Seismic anomalies in the asthenosphere (A) and at the base of the mantle, just above the core (B); the anomalies are relative to a one-dimensional reference model. The correlation between hot spots (triangles) and the edges of the slow (red) anomalies in the lower mantle has been used to argue that hot spots originate from plumes at these depths. However, hot spots correlate as well if not better with slow-wave speed anomalies in the asthenosphere, the region where the lavas originate.

of low-wave speed, low-viscosity anisotropic material that is consistent with the observed properties of the asthenosphere (12). Interaction of seismic waves with this material perturbs the material and further reduces the seismic wave speed (12). Density measurements of volatile-containing alkali basalts show that these melts are neutrally buoyant at the pressure and temperature conditions of the asthenosphere under continents (10), adding to the evidence that the asthenosphere is a zone of partial melt. Because both seismic and mechanical properties are used to describe the asthenosphere, the bottom boundary remains poorly defined.

There is also evidence that the asthenosphere is hotter than the mantle below it (2, 4, 13). Average temperature profiles from three-dimensional global mantle convection simulations show a local thermal maximum beneath the lithosphere because of the insulating properties of the tectonic plates (4, 13). This increase in temperature can reduce the mechanical strength, lower the seismic wave speed, and eliminate the need to bring heat directly from Earth's core to the asthenosphere to explain volcanic activity at hot spots. The hottest regions in the asthenosphere

may be as much as 200°C warmer than beneath mid-ocean ridges (4) and even hotter than the core-mantle boundary, when corrected for adiabatic cooling (the cooling that results from transporting material from high to low pressure). This is important because the asthenosphere is at or near its melting point, and a large temperature increase would thus produce a substantial amount of melt. Most researchers have assumed that the hottest material should be below ridges, leading them to invoke plumes to explain 200°C lateral temperature variations. Yet in the mantle, where a substantial fraction of the heat is generated by the decay of radiogenic elements, such lateral variations in temperature can arise without the need to deliver heat from the deep mantle via a plume (4).

Further information on mantle temperature comes from absolute seismic wave speeds, which can be coupled with a thermodynamic description of mantle minerals to estimate temperature. This approach confirms that the asthenosphere is anomalously hot, whereas the deep mantle is anomalously cold (14). Thus, the highest temperatures in the asthenosphere can be greater than

those of the deep mantle, and magmas from beneath ridges can erupt at lower temperatures than magmas extracted from the asthenosphere beneath the middle of large plates.

Whereas Earth's interior has traditionally been viewed as a series of uniform layers, seismic tomography has enabled mapping of complex three-dimensional structures. French *et al.* (3) have resolved horizontally elongated, low-wave speed structures at depths of 200 to 350 km extending from the East Pacific Rise to the middle of the Pacific plate; they found similar features beneath other oceans. These low-wave speed structures occur below the average depth of the asthenosphere and represent the interaction of broad, passive upwellings with the base of the asthenosphere. Most hot spots occur above these low-wave speed regions (see the figure, panel A), and the correlation between hot spots and the edges of the low-shear velocity large structures at the core (see the figure, panel B)—a recent observation used to support the existence of deep mantle plumes—is no better than the correlation with the low-wave speed regions beneath the asthenosphere (15).

Plate tectonics and midplate volcanoes are the natural results of processes in the asthenosphere and lithosphere of the cooling Earth.

Given that the hottest part of the mantle lies directly beneath the lithosphere (2, 4, 13), there is no need for heat from the core to be carried up in narrow plumes (4). As a result, the asthenosphere is by far the largest, most accessible, and most plausible source for hot spot magmas. Although many authors have ruled out this obvious source on the basis of geochemical assumptions, it is not ruled out by any data or theory. ■

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10.1126/science.1261831



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Science **346**, 1184 (2014);
DOI: 10.1126/science.1261831

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