

mis of most land plants is uniseriate (comprising one layer), and if SHR and SCR orthologs control development in these species, this mechanism may have evolved early in the history of land plants. But there are some rare exceptions. For example, extant members of the Equisetales (horsetails), whose forebears were important species in Carboniferous forests 300 million years ago, have two layers of endodermis in some organs (8). These horsetails have apparently tinkered with their *SCR* and *SHR* genes to allow SHR to escape the clutches of SCR in the first endodermal layer, thus extending the endodermis to further layers.

Why is the structure of a single-layered endodermis so conserved across most land

plants? Autotrophic plants rely on the uptake of nutrients and water from the soil, so tight spatial regulation of endodermal development reflects its significance. The endodermis is highly specialized in that intercellular spaces between the cells are sealed, prohibiting the free diffusion of water and ions through the interstices. If water and ions are to pass through this roadblock, they must do so in a regulated manner, via the cytoplasm of endodermal cells. This affords strict control over transport and may well have provided a survival advantage—the highest level of control over a specialized tissue of very limited size. If so, this discovery may explain the evolution of a tightly regulated developmental program in

angiosperms (flowering plants) and also points to changes in developmental programs that may have occurred during the past 470 million years of land plant evolution.

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GEOCHEMISTRY

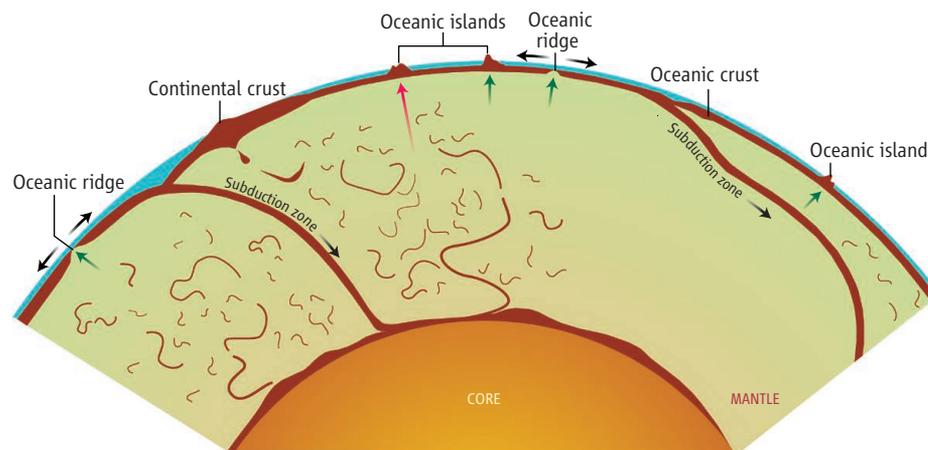
Food for a Volcanic Diet

Claude Herzberg

Volcanic eruptions have the power to reshape Earth's landscape, alter climate, and affect life. To understand how this works requires that we go deep into the Earth to learn exactly what kind of rock melts to produce magmas and the chemistry of this source rock. These are fundamental problems in geology, and they are also among the most difficult to understand. On page 412 in this issue, Sobolev *et al.* (1) describe a method for identifying some of these source rocks. We can think of them as food for volcanoes in the sense that they melt to provide the magmas that can erupt to the surface. To understand what Sobolev *et al.* have done and the ramifications that go beyond Earth science, we need to start with a refresher in geology.

Earth's mantle consists mostly of peridotite, a rock rich in the mineral olivine $(\text{Mg,Fe})_2\text{SiO}_4$. When peridotite partially melts, the liquids collect to magmas that rise to the crust, give off gases like SO_2 , CO_2 , and H_2O , and solidify to basalt, a rock rich in the minerals clinopyroxene $[\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6]$ and plagioclase $[(\text{Ca,Na})(\text{Al}_{1-2}\text{Si}_{2-3})\text{O}_8]$. Portions of these outer layers can be recycled back into the mantle at subduction zones and below thickened continents (see the figure). The recycled basaltic crust is transformed to a new rock called pyroxenite, so-called because it is rich in clinopyroxene. It may pile up on Earth's core, or be mixed back into the mantle with structures that have

Chemical analyses of lava can now reveal the nature of the rocks deep in the Earth that melted and rose to generate specific volcanoes.



Models of Earth's crust and mantle. Oceanic crust (brown) is solidified liquid that forms by partial melting of mantle peridotite (green) at oceanic ridges; together with sediment, oceanic crust can be recycled back into the mantle at subduction zones (2, 3, 6). Continental crust (brown) forms at subduction zones and can be recycled when it thickens by delamination (5, 15). All crust (brown) is transformed to pyroxenite (brown) when recycled. Green arrow denotes melting peridotite. Red arrow denotes melting pyroxenite. Recycled crust may be distributed uniformly throughout the mantle, or it may be concentrated in certain hemispheres or depths. Crustal thickness is exaggerated for clarity, but ranges from ~6 to 40 km at the present time. Recycling is expected to reduce crust to dimensions ranging from micrometers to kilometers.

been described as marble cake (2), plum pudding (3), spaghetti (4), and gumbo (5) (see the figure). Volcanoes like those of Hawaii can melt from source rocks consisting of peridotite and/or pyroxenite from recycled crust. Sobolev *et al.* describe a method for identifying this rock based on the chemistry of lavas on volcanoes.

Sobolev *et al.* determined that many volcanoes melted from recycled crust, a conclusion that is not new (6). However, there has always been some ambiguity with past methods of identifying recycled crust based on the isotope

and trace-element geochemistry of lavas at the surface. New interpretations suggest that many oceanic islands melted from mantle peridotite that had been modified by melts that flowed through it (7, 8), a process called metasomatism (9). Because it makes no difference to an atom of lanthanum, for example, whether it ends up concentrated in the crust or as metasomatized peridotite, using it as a tracer can be ambiguous and nonunique (7, 8).

A breakthrough came when Sobolev *et al.* (10) showed that the nickel contents of many

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olivine crystals in Hawaiian lavas were higher than those expected from melts of peridotite, and they preferred to explain this with a recycled crust source instead. But a lingering ambiguity is that a high nickel content in olivine can also arise when peridotite is enriched in pyroxene by melt-rock reaction (11). Supporting evidence for the recycled-crust interpretation (10) comes from the calcium contents of the Hawaiian lavas, which are too low to be easily explained by melting peridotite (12). Nickel and calcium are therefore telling the same story. That is, the main shield-building lavas at Hawaii were melted from a pyroxenite source rock that required the involvement of recycled crust as proposed by Sobolev *et al.* (10). The authors go further in that they examine the problem that arises when nickel, calcium, and manganese are used, and they extend the analysis to a larger population of volcanoes. Their results, together with other recent studies (7, 8, 11), show that it is unlikely that a single rock type will be an appropriate source for all oceanic volcanoes. For example, recycled

crust is an important source rock for the Hawaiian islands (1, 10, 12), whereas metasomatized peridotite is the source rock for the Cook islands (7). An outstanding question is whether peridotite sources become metasomatized by melted recycled crust (13) or in some other way (7, 8).

Future studies might allow us to transform our picture from hypothetical models to actual three-dimensional views showing the size and distribution of recycled crust in the mantle. The implications go far beyond geology. For example, it may be no surprise that Sobolev *et al.* (1) identify pyroxenite as the rock that melted to produce the Siberian Traps. This was a magmatic flood on land so massive in scale that it triggered the largest mass extinction of life on Earth, some 250 million years ago (14). Although the exact causal links remain poorly understood in detail, one can reasonably imagine a different outcome if the mantle diet had less pyroxenite and more peridotite. Under these circumstances, less magma would have been pro-

duced and made available for eruptive flooding, and Earth's biosphere could have evolved along different pathways.

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BIOCHEMISTRY

An Ancient and Intimate Partnership

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Before the evolution of photosynthesis ~3.5 billion years ago, Earth's atmosphere was reducing, and iron was mainly in its Fe(II) oxidation state. The abundant Fe(II) soaked up the early molecular oxygen generated by photosynthesis. Complex multicellular organisms could not evolve until substantial amounts of oxygen became available in Earth's atmosphere ~2 billion years ago. Then the tables were turned: Organisms used Fe(II) to access the oxidative power of molecular oxygen, thus dramatically increasing the efficiency of metabolic energy generation.

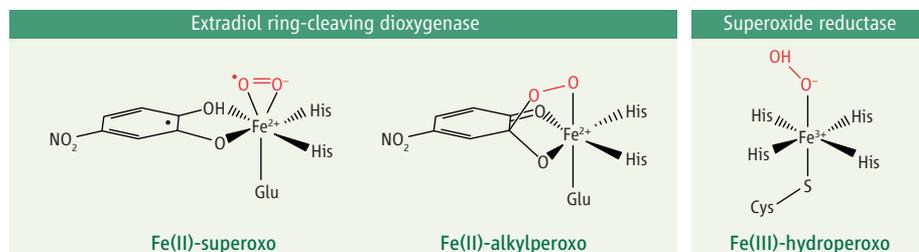
Two reports in this issue highlight the biological intimacy of the relation between Fe(II) and dioxygen. On page 453, Kovaleva and Lipscomb (1) show how an enzyme fine-tunes the properties of Fe(II) to activate O₂, thereby enabling the oxidation of aromatic diols in a four-electron metabolic process. However, the by-products of molecular oxygen reduction

can be highly toxic and need to be removed rapidly. On page 449, Katona *et al.* (2) reveal details of how one enzyme helps to remove the most toxic by-product, superoxide, by reducing it to the less toxic hydrogen peroxide.

Kovaleva and Lipscomb report on the bacterial extradiol ring-cleaving dioxygenase, a key enzyme in the metabolic degradation of aromatic hydrocarbons introduced into soil by humans. The enzyme contains a mononuclear Fe(II) bound to two histidines and a carboxylate, a motif that has evolved several times in different enzymes that catalyze crucial

Nonheme iron enzymes can catalyze a wide variety of chemical reactions. Two studies show how this versatility is achieved.

chemistries in the synthesis of neurotransmitters, antibiotics, and plant hormones (3). The authors added an inefficient substrate (with a slow conversion rate) to the crystallized enzyme in an O₂-depleted atmosphere. By rapidly freezing the crystal, they were able to simultaneously trap three different steps in the catalyzed reaction. Iron acts as a conduit to enable electron density to move from the aromatic substrate to dioxygen. This transfer creates two reactive species: a superoxo and a substrate radical. The superoxo species is bound side-on to the iron, but the interaction is weak



Iron-dioxygen relationships. Mononuclear nonheme iron enzymes can accommodate a diverse range of geometries with substrates and dioxygen, as illustrated here by the trapped catalytic intermediates in an extradiol ring-cleaving dioxygenase (left and center) reported by Kovaleva and Lipscomb and in superoxide reductase (right) reported by Katona *et al.*

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