GEOCHEMISTRY

The Origin of Alkaline Lavas

Alkali-metal-rich lavas on ocean islands are produced from veins that form in oceanic mantle lithosphere as it ages.

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Alkaline lavas—mantle-derived magmas rich in alkali metals such as potassium and sodium—are commonly found in the interiors of tectonic plates, both on continents and on islands in ocean basins. Melting of metasomatic materials in the mantle lithosphere has long been conjectured to be the main source of these magmas (1, 2), but this has not been successfully simulated experimentally. On page 916 of this issue, Pilet et al. (3) report experiments that explain the properties of alkaline magmas in a simple and elegant way.

Oceanic crust forms at mid-ocean ridges, where tectonic plates move apart. As it moves further away from the ridge, the lithosphere thickens, reaching its full thickness after about 70 million years (see the figure, left panel). It has long been widely accepted that the oceanic crust—after recycling into the deep mantle through subduction—becomes the source of alkali-rich melts needed to explain the compositions of

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ocean island basalts (4), but this explanation has been criticized and remains debated (5–7). One of the problems is that melting of the oceanic crust would lead to silica-rich rather than alkaline melts.

Pilet et al. now show that melting not of recycled oceanic crust but of metasomatic veins in the lithosphere produces melts with elemental compositions matching those of extreme alkaline lavas (nephelinites). When these nephelinite melts interact with the host peridotites, they produce modified melts that form a compositional spectrum from less extreme alkaline lavas (basanites) to the more common alkali basalts. The veins consist of amphiboles, a group of minerals that are stable in the lithosphere but not in the seismic low-velocity zone (LVZ). Thus, the results provide convincing evidence for a lithospheric origin of alkaline magmas.

The key question concerns the origin of metasomatic amphibole-rich veins. The volatile- and alkali-rich character of amphibole-rich veins requires that they crystallize in the lithosphere from small-

mass-fraction (low-degree) melts that ultimately originated in the LVZ—a process called mantle metasomatism. As Pilet et al. explain, these low-degree melts can be produced in regions deeper than and in the vicinity of ocean ridge mantle melting [figure S5 in (3)]. Such melts may in fact exist throughout the LVZ (see the figure, left panel) (5, 8, 9), causing the observed low seismic velocity (8). Because of their buoyancy, such low-degree melts tend to concentrate toward the top of the LVZ and are enriched in volatiles (such as water and carbon dioxide) and in "incompatible" elements (such as Ba, Rb, Th, U, Nb, and light rare earth elements) that prefer to enter the melt over solid minerals.

However, metasomatic amphibole-rich veins in the lithosphere do not melt without thermal perturbation. Hot "plume" melts from the deep mantle may cause the veins to melt; mixing of the two melts in different proportions then results in the alkali-rich nature and compositional spectrum of ocean island lavas (see the figure, right panel).

The lithosphere does not reach its full
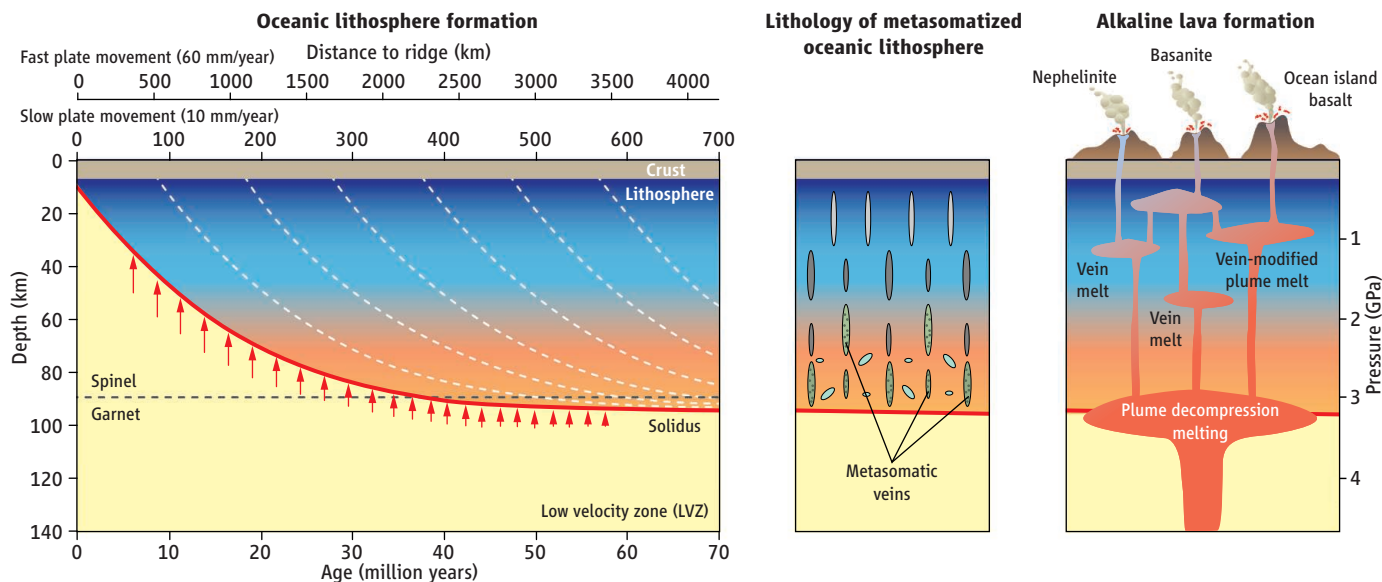
From oceanic lithosphere formation to alkaline lavas. (**Left**) Oceanic lithosphere grows with time by accreting LVZ material at the base (red arrows), taking ~70 million years to reach its full thickness. The thick red curve is the present-day lithosphere-LVZ interface, which is a natural solidus (the boundary between some melting and no melting). The thin white dashed curves indicate where this interface was in the past, illustrating the continuing lithosphere growth with time as the plate ages. (**Middle**) Close-up of metasomatic veins in the surrounding peridotite. Going upward, the veins are garnet pyroxenite, hornblende pyroxenite and hornblendite. The veinlets at the top are dunite inherited from ridge melting. (**Right**) When the mature oceanic lithosphere is reheated due to a hot plume rising up from deeper in the mantle, the vein melt. The vein melts may be altered through addition of surrounding material and mixing with plume melt. The degree of mixing determines which type of alkaline magma is formed and erupted.

thickness until it is ~70 million years old; mantle metasomatism thus continues during this time. This is equivalent to a distance of 700 km from the ridge if the plate spreads slowly at 10 mm per year and of 4200 km from the ridge if the plate spreads fast at 60 mm per year (see the figure, left panel). Hence, the oceanic lithosphere is a large geochemical reservoir enriched in alkalis, volatiles, and incompatible elements.

Alkaline lavas on ocean islands only sample very small amounts of amphibole-rich veins that may be ubiquitous throughout the oceanic lithosphere (see the figure, middle panel). Recycling of such metasomatized lithosphere into the deep mantle over much of Earth's history will cause mantle compositional heterogeneities on all scales. Involvement of such enriched heterogeneities in mantle source regions can account for the enriched characters of ocean island basalts (5).

Amphiboles are important minerals. A type of amphibole called pargasite may be the key mineral that determines the thickness of the mature oceanic lithosphere and the nature of the LVZ. Experimental studies suggested long ago that the lithosphere-to-LVZ transition may be a petrologic transition from solid pargasite-bearing peridotite to peridotite containing a small melt fraction (~1%) (8, 9). This argument suggests that the mature oceanic lithosphere should be less than 95 km thick (8)—too thin for models in the 1970s (10) but consistent with more recent geophysical observations and models (11).

Although melting of amphibole-rich veins can also explain nephelinite lavas on land (3), further effort is needed to explain alkaline magmas such as kimberlite, lamproite, carbonatite, some nephelinite and their associations in continental settings with thick lithospheric roots (12). Their origin is apparently associated with metasomatized continental lithosphere (12). Kimberlite melts may actually originate at great depths, perhaps in the transition zone between the upper and lower mantle (13), and may be the agent that metasomatizes the continental lithosphere (14). Metasomatic vein amphiboles are potassium-rich (3), and potassium-amphiboles can be stable up to 16 GPa in the subducting oceanic lithosphere (15) before they undergo dehydration melting in the transition zone. It is possible that such melts, in the presence of carbon dioxide, are of kimberlitic composition, thus offering new perspectives on the origin of continental alkaline magma associations.

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To Be or Not to Be Localized

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The hole created by emission of a core electron in a diatomic molecule resides in an entangled state.

In molecules, valence electrons form molecular bonds, whereas the underlying core electrons play a supporting role. If a vacancy, or hole, is created in the core orbitals by an excitation process, a rearrangement process called Auger decay can occur: A valence electron drops to fill the core hole, and energy is released by emitting an Auger electron from another valence orbital. It has long remained unclear whether this short-lived core hole in a homonuclear diatomic molecule such as N_2 is localized on one atomic site, or delocalized over both. On page 920 of this issue, Schöffler *et al.* (1) show that this question cannot be answered without taking into account how the unstable core hole state relaxes by Auger decay. They show that the photoelectron and the Auger electron that are emitted form an entangled state. Whether one finds the core hole to be localized or

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delocalized will depend on the experiment used to observe this entangled state.

To answer the question about core hole localization and delocalization experimentally has required the development of sophisticated spectroscopic methods, but this question was first addressed theoretically decades ago. The direct core hole calculation of O_2 within the Hartree-Fock approximation supported a localized core hole picture. The energy of a symmetry-broken ionic state of O_2, in which a core hole is localized and thus the O atoms are inequivalent, is lower and agrees better with the experimental value than does the delocalized state (2). However, according to the Green's function approach, which includes more electron correlations, the energy difference between the localized and delocalized core holes calculated within the Hartree-Fock approximation is attributed to the neglect of electron correlations (3), and so at this level of theory, it is not possible to decide which description of the core holes

better accommodates the experiments.

Core hole localization and delocalization can be built into theoretical calculations, but is it likely that we could see the localization and delocalization experimentally? State-of-the-art ab initio calculations (4, 5) predicted that the two delocalized core hole states of N_2^+, which have different symmetries, are different in energy by ~0.1 eV. This energy gap, which is not seen for the symmetry-broken localized holes, is referred to as gerade-ungerade splitting. When all electron coordinates change sign, a gerade (even) wave function stays the same, but an ungerade (odd) wave function changes sign. Also the equilibrium bond length would differ by ~0.04 pm between gerade and ungerade core hole states (4, 5).

If such energy gap and different bond lengths can be observed, they could be considered as experimental evidence for delocalized core holes. Recent high-resolution photoelectron spectroscopy studies confirmed the gerade-ungerade splitting (6) and