Where Do Carbon Atoms Reside Within Earth's Mantle?

Solubility measurements of carbon in olivine confirm a widely held belief that most carbon is stored in other, less abundant minerals.

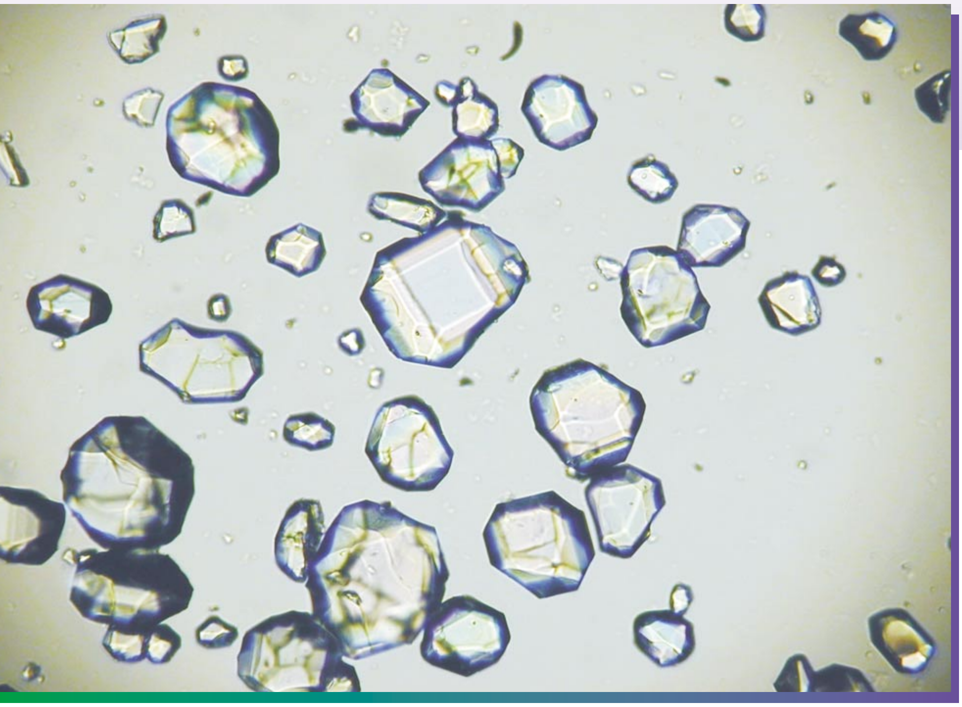
Earth scientists routinely monitor the levels of carbon they find in the planet's biomass, atmosphere, and oceans. But to judge by the composition of basaltic magma and the flux of carbon dioxide coughed out by volcanoes, the amount of carbon sequestered within Earth's voluminous mantle—estimated to be a few hundred parts per million (ppm) by weight—is roughly a thousand times larger than the amount on the surface. The presence of so huge a reservoir of carbon separated by mere kilometers from the comparatively tiny one on the surface has spurred researchers to figure out where and in what form the carbon is stored within Earth's interior.

As the dominant constituent of the upper 400 km of the mantle, olivine is a natural suspect. It is a solid mixture of 90% magnesium silicate and 10% iron silicate. Like any ionic mineral, it accepts small levels of impurities into the crystal structure. In the case of carbon, C^{4+} ions could substitute into tetrahedral Si^{4+} vacancies, for instance, although the radius mismatch between carbon and silicon cations would make the fit energetically unlikely. Substitution of carbon into magnesium vacancies is harder to imagine; no stable C^{2+} defect has ever been observed as an ionic substituent, probably because of its partially filled valence-electron shell in that charge state. Other possibilities come to mind, though: carbon diffusing into interstitial sites or line defects that could accommodate impurity ions.

Unfortunately, trace amounts of carbon in rock are hard to measure. The ubiquity of contaminant hydrocarbons in labs and the slow diffusion of carbon in silicates stymied experimenters in the mid-1980s. Typically, researchers took olivine from xenoliths—inclusions that make their way to the surface inside volcanic rock. Hoping to ensure carbon-saturated samples, the researchers annealed the olivine at high pressure and temperature in the presence of a carbon-bearing phase. Reports of the solubility from competing groups varied widely. At the parts-per-million level, measurements must be ultrasensitive: The touch of a ChemWipe™, fingerprint, or even stray atoms from the lubrication in a vacuum pump could ruin an experiment.

Made to measure

Hans Keppler and his student Svyatoslav Shcheka, both at the University of Tübingen, Germany, have now resolved the lingering uncertainty by pursuing a different tack.[1] Instead of measuring carbon squeezed into olivine chunks spewed from volcanoes, Keppler made his own proxy under conditions that would maximize the amount of carbon absorbed within the crystal. The recipe is simple enough: Take a stoichiometric mixture of magnesium oxide and silicon dioxide, 1% water by weight, and cook at gigapascal pressures and 1200°C mantle temperatures in a carbonate-rich melt. Such melts are thought to be common within Earth's mantle. Using that recipe he produced the crystals of forsterite (90% of the solid mixture that makes up olivine), pictured on page 22. To distinguish dirt from carbon dissolved in the silicate, Keppler grew his crystals in



Crystals of synthetic forsterite, the magnesium-dominant member of the olivine group. Olivine is the most abundant mineral within Earth's upper mantle. (Courtesy of Hans Keppler.)

carbonate made from carbon-13, which is 1% as abundant in nature as carbon-12. That gained him 100 times greater sensitivity.

To determine how much ^{13}C had diffused into the forsterite, Keppler turned to Michael Wiedenbeck, a geochemist at the GeoForschungsZentrum in Potsdam, Germany. After eliminating sources of carbon from the vacuum system, Wiedenbeck used secondary-ion mass spectroscopy (SIMS) in ultrahigh vacuum to measure the ratio of ^{28}Si to ^{13}C. In that technique, energetic cesium ions collide with surface atoms and kick out secondary ions, which are accelerated into a magnetic field that filters the ions by mass. For carbon, this approach is tricky. Carbon's half-filled outer shell makes the atom reluctant to accept or give up electrons and form secondary ions.

SIMS is a comparative technique, and because the collection efficiency depends on which trace elements are measured, the need for a reference standard is paramount. Keppler therefore measured both carbon-free and carbon-saturated crystals. Borrowing a technique from semiconductor science, he implanted a known dose of ^{13}C into the carbon-free crystals to create a calibration standard.

By comparing several crystals grown at pressures up to 3.5 GPa with the known standard, Wiedenbeck found that carbon solubility in forsterite never exceeded 1 ppm by weight. Adding iron to the mix did not significantly alter the solubility. The results indicate that the vast reservoir of carbon atoms simply cannot be stuffed into the most common minerals within the mantle. So, carbon must reside either in reduced elemental form as graphite or diamond, or within a CO_2-rich carbonate phase.

Moving atoms through the mantle

The remoteness of the mantle limits geologists to studying the carbon concentrations in xenoliths and volcanic rock. The rarity of graphite and diamond in existing samples may mirror their low concentrations in the mantle. Says Keppler, "Even the highest grade ore from a kimberlite [diamond] mine only contains 1 carat of diamond per ton of rock, [roughly] 0.2 ppm, negligible compared to a mantle abundance of carbon on the order of 100 to 1000 ppm."

If CO_2-rich carbonate phases host most of the carbon in Earth, as Keppler argues, the implications for the global carbon cycle may be profound. The mantle is a dynamic environment. Differences in mineral composition, temperature, and pressure largely determine what melts. Carbonates have low melting points and their melts have extremely low viscosity. To appreciate the effect on transport within the mantle, consider what happens when melting occurs. Experts suppose that the melt initially percolates along grain boundaries and, being more buoyant than dense rock, flows upward through cracks and fissures, much like water in an aquifer. During migration, the melt can pick up as much as 10–20% of its weight as carbon. At shallower depths, with pressures between 2 and 3 GPa, a carbonate melt decomposes to liberate carbon in the form of a free CO_2 fluid. The mobility of that CO_2 can lead to selective enrichment of mantle reservoirs. Were the carbon to be locked up in the olivine, which participates little in mantle melting, such a mobile phase would be unlikely to form.

The solubility of volatiles like CO_2 in magma is so low that further depressurization eventually leads to a stage in which CO_2 prefers a gaseous phase. The degassing from basalt and erupted lava prevents researchers from directly measuring the original amounts of water and CO_2 in magma, except in deep mid-ocean ridges. There, the temperatures and pressures limit the degassing and confine volatiles within the lava. The concentrations found from "pillow flow" lavas and melt inclusions in a deep ridge off the Mexican coast (the Siqueiros Transform fault), for instance, indicate a wide variation in the concentration of CO_2 reservoirs, from 44 to 244 ppm.[2] But the extent and depth of those reservoirs could be as important as their concentrations of volatile fluids.

There is plenty of evidence that the mantle is highly heterogeneous, although the spatial scale of the heterogeneities is unknown. Derrill Kerrick of the Pennsylvania State University argues that the release of CO_2 and water from subducted slabs may vary from one subduction zone to another, and the presence of hot spots and plume heads in the mantle could be mechanisms for concentrating volatiles within pockets underground. (See PHYSICS TODAY, August 1999, page 21 for a discussion of the Lava-lamp model.)

Keppler speculates that a large melting event could tap into such a reservoir and spew out enough CO_2 to affect climate change and trigger "super greenhouse" conditions. He cites models that link enormous so-called flood basalt eruptions to global extinction events like the one at the boundary of Earth's Triassic and Jurassic eras 200 million years ago.[3]

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References

1. H. Keppler, M. Wiedenbeck, S. S. Shcheka, *Nature* **424**, 414 (2003).
2. A. E. Saal, E. H. Hauri, C. H. Langmuir, M. R. Perfit, *Nature* **419**, 451 (2002).
3. A. Marzoli et al., *Science* **284**, 616 (1999).