

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 in-

stance, 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

1
Hydrogen
1.00794
0.999
-252.87

2
Helium
4.0026
0.0005
-268.93

3
Lithium
6.941
0.054
180.5

4
Beryllium
9.0122
1.85
1287

5
Boron
10.811
2.46
2078

6
Carbon
12.011
2.27
3500

7
Nitrogen
14.007
1.261
192.5

8
Oxygen
15.999
1.429
183.0

9
Fluorine
18.998
1.681
188.1

10
Neon
20.180
0.003
244.6

11
Sodium
22.990
0.97
97.7

12
Magnesium
24.305
1.74
650

13
Aluminum
26.982
2.70
933

14
Silicon
28.086
2.33
1414

15
Phosphorus
30.974
2.99
44.2

16
Sulfur
32.065
3.17
115.7

17
Chlorine
35.453
3.14
-34.04

18
Argon
39.948
1.781
-185.85

19
Potassium
39.098
0.86
63.1

20
Calcium
40.078
1.55
842

21
Scandium
44.956
47.867
1511

22
Titanium
47.867
4.51
1668

23
Vanadium
50.942
6.11
1910

24
Chromium
51.996
7.14
1907

25
Manganese
54.938
7.47
1538

26
Iron
55.845
7.87
1538

27
Cobalt
58.933
8.91
1495

28
Nickel
58.693
8.92
1455

29
Copper
63.546
8.96
1083.4

30
Zinc
65.39
7.14
419.5

31
Gallium
69.723
5.34
29.76

32
Germanium
72.61
5.32
231.9

33
Arsenic
74.922
5.73
211.7

34
Selenium
78.96
4.82
217.3

35
Bromine
79.904
3.12
-7.2

36
Krypton
83.80
3.17
-153.22

37
Rubidium
85.468
1.53
39.3

38
Strontium
87.62
2.63
-77.7

39
Yttrium
88.906
4.47
1521

40
Zirconium
91.224
6.51
1855

41
Niobium
92.906
8.57
2471

42
Molybdenum
95.94
10.28
2623

43
Technetium
98.906
11.5
2150

44
Ruthenium
101.07
12.37
2334

45
Rhodium
102.91
12.45
1964

46
Palladium
106.42
10.49
1554.3

47
Silver
107.87
19.3
961.8

48
Cadmium
112.41
8.65
321.1

49
Indium
114.82
7.31
156.6

50
Tin
118.71
7.31
231.9

51
Antimony
121.76
6.70
630.6

52
Tellurium
127.60
6.24
221.9

53
Iodine
126.91
4.94
113.7

54
Xenon
131.29
5.887
108.02

55
Cesium
132.91
1.96
28.4

56
Barium
137.33
1.87
777

57-70
Lanthanoids

57
Lanthanum
138.91
6.14
920

58
Cerium
140.12
6.88
795

59
Praseodymium
140.91
6.94
935

60
Neodymium
144.24
6.88
1021

61
Promethium

62
Samarium
150.36
7.26
1100

63
Europium
151.96
5.44
1072

64
Gadolinium
157.25
8.26
1312

65
Terbium
158.93
8.26
1356

66
Dysprosium
162.50
8.26
1407

67
Holmium
164.93
8.26
1461

68
Erbium
167.26
8.26
1497

69
Thulium
168.93
8.26
1515

70
Ytterbium
173.04
6.4
821

71
Lu
174.97
13.01
1609

72
Hf
178.49
10.28
1572

73
Ta
180.95
10.28
1569

74
W
183.84
19.3
3422

75
Re
186.21
21.02
3443

76
Os
190.23
22.62
3071

77
Ir
192.22
22.62
2446

78
Pt
195.08
21.06
1962.4

79
Au
196.97
19.3
1063.4

80
Hg
200.59
10.38
-38.83

81
Tl
204.38
11.83
304

82
Pb
207.2
11.34
271.3

83
Bi
208.98
9.78
271.3

84
Po

85
At

86
Rn

87
Fr

88
Ra

89-102
Actinoids

89
Actinium
227.03
13.7
1020

90
Th
232.04
15.37
1944

91
Pa
231.04
15.37
1569

92
U
238.03
19.3
1146

93
Np
237.04
16.7
1116

94
Pu
244.06
19.3
1004

95
Am
243.06
15.1
1116

96
Cm
247.07
16.7
1116

97
Bk

98
Cf

99
Es

100
Fm

101
Md

102
No

Periodic Table of the Elements

March 2003

Element Name

Atomic No.

Symbol

Atomic weight

Density

M.p./B.pt.(°C)

Solids & Liquids (g/cm³) Gases(g/l)

Melting point (Solids & Liquids) - Boiling point (Gases)

Standard Catalog Items

13 Boron

14 Carbon

15 Nitrogen

16 Oxygen

17 Fluorine

18 Neon

19 Potassium

20 Calcium

21 Scandium

22 Titanium

23 Vanadium

24 Chromium

25 Manganese

26 Iron

27 Cobalt

28 Nickel

29 Copper

30 Zinc

31 Gallium

32 Germanium

33 Arsenic

34 Selenium

35 Bromine

36 Krypton

37 Rubidium

38 Strontium

39 Yttrium

40 Zirconium

41 Niobium

42 Molybdenum

43 Technetium

44 Ruthenium

45 Rhodium

46 Palladium

47 Silver

48 Cadmium

49 Indium

50 Tin

51 Antimony

52 Tellurium

53 Iodine

54 Xenon

55 Cesium

56 Barium

57-70 Lanthanoids

57 Lanthanum

58 Cerium

59 Praseodymium

60 Neodymium

61 Promethium

62 Samarium

63 Europium

64 Gadolinium

65 Terbium

66 Dysprosium

67 Holmium

68 Erbium

69 Thulium

70 Ytterbium

71 Lu

72 Hf

73 Ta

74 W

75 Re

76 Os

77 Ir

78 Pt

79 Au

80 Hg

81 Tl

82 Pb

83 Bi

84 Po

85 At

86 Rn

87 Fr

88 Ra

89-102 Actinoids

89 Actinium

90 Th

91 Pa

92 U

93 Np

94 Pu

95 Am

96 Cm

97 Bk

98 Cf

99 Es

100 Fm

101 Md

102 No

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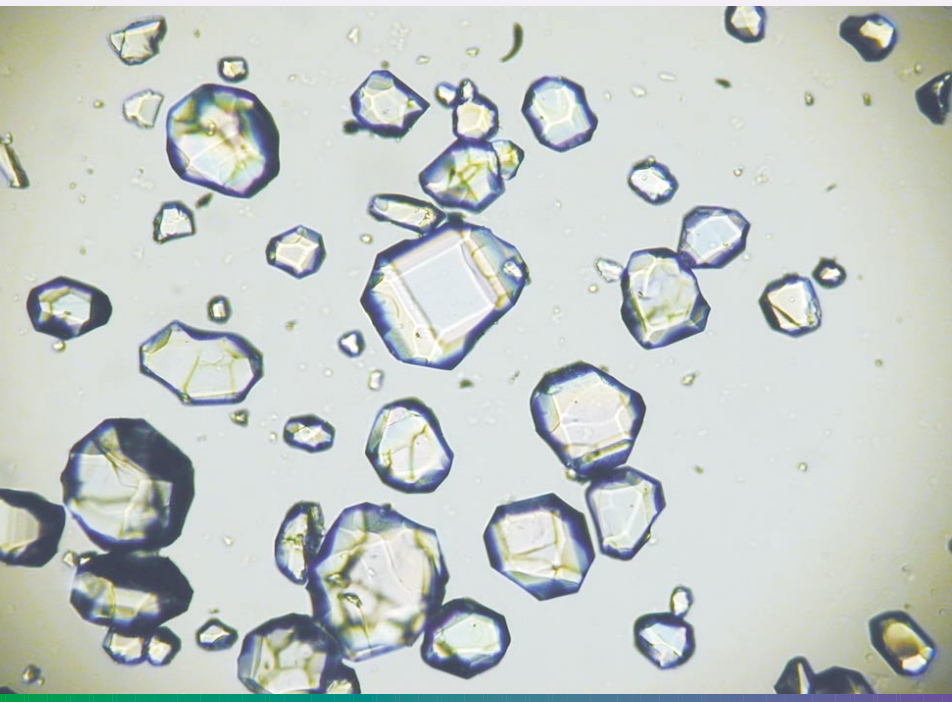
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Crystals of synthetic forsterite, the magnesium-dominant member of the olivine group. Olivine is the most abundant mineral within Earth's upper mantle. (Courtesy of Hans Keppler.)

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 ultra-high 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 reser-

voir 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

Mark Wilson

References

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