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Carbon solubility in mantle minerals

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Abstract

The solubility of carbon in olivine, enstatite, diopside, pyrope, $MgAl_2O_4$ spinel, wadsleyite, ringwoodite, $MgSiO_3$–ilmenite and $MgSiO_3$–perovskite has been quantified. Carbon-saturated crystals were grown from carbonatite melts at 900–1400 °C and 1.5 to ~ 26 GPa in piston cylinder or multi-anvil presses using carbon enriched to >99% in the ^{13}C isotope. In upper mantle silicates, carbon solubility increases as a function of pressure to a maximum of ~ 12 ppm by weight in olivine at 11 GPa. No clear dependence of carbon solubility on temperature, oxygen fugacity or iron content was observed. The observation that carbon solubility in olivine is insensitive to oxygen fugacity implies that the oxidation state of carbon in the carbonatite melt and in olivine is the same, i.e., carbon dissolves as C^{4+} in olivine. Carbon solubility in spinel $MgAl_2O_4$, transition zone minerals (wadsleyite and ringwoodite), $MgSiO_3$–ilmenite and $MgSiO_3$–perovskite are below the limit of detection of our SIMS-based analytical technique (i.e., below 30–200 ppb by weight). The differences in carbon solubilities between the various minerals studied appear to correlate with the polyhedral volume of the Si^{4+} site, consistent with a direct substitution of C^{4+} for Si^{4+}. These results show that other, minor carbon-rich phases, rather than major, nominally volatile-free minerals, dominate the carbon budget within the bulk Earth's mantle. A significant fraction of total carbon could only be stored in silicates in a thin zone in the lowermost upper mantle, just above the transition zone, and only if the bulk carbon content is at the lower limit of published estimates. The carbon budget of the remaining mantle is dominated by carbonates and possibly diamond. The low melting point of carbonates and the high mobility of carbonate melts suggest that carbon distribution in the mantle may be highly heterogeneous, including the possibility of massive carbon enrichments on a local scale, particularly in the shallow subcontinental mantle.
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1. Introduction

Only a small fraction of the total carbon budget of our planet is located in near-surface reservoirs [1,2]. Although some carbon might be stored in the core [3,4], the mantle is thought to be the Earth's largest carbon reservoir [5].

Carbon may be stored in the mantle as carbonates, graphite, diamond or as C–H–O fluids [6]. Carbon-bearing fluids in the mantle are usually dominated by CO_2, but under very reducing conditions, CH_4 may also become important. Alternatively, traces of carbon may be dissolved in common, nominally volatile-free silicates. A significant solubility of carbon in mantle silicates is suggested by fluid inclusions. Brewster in 1823 [7] first

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observed the ubiquitous presence of tiny (<1 μm) bubbles in minerals from peridotite xenoliths in alkali basalts. The bubbles were filled with "a mysterious fluid with remarkable physical properties," later identified as nearly pure liquid carbon dioxide [8,9]. These observations were interpreted as evidence that such C-rich inclusions formed by the exsolution of carbon dioxide [10,11], originally dissolved in host minerals at higher pressure. Alternatively, they may represent fluid trapped during crystal growth from a melt or during subsequent healing of fractures in crystals [12,13]. Four observations support the former interpretation: (1) The bubbles are extremely small; (2) they are located on dislocations or other defects in the crystal structure; (3) they are concentrated on the boundaries of inclusion-free recrystallized grains [10]; and (4) the bubbles appear to dissolve into the host olivine at pressures up to 110 kbar during annealing experiments [14].

Green and Guegen [11] estimated that the volume fraction of carbon dioxide inclusions in olivine from a peridotite xenolith in a kimberlite corresponds to a carbon solubility of 160 ppm by weight (ppmw), assuming a positive pressure dependence of solubility. Comparing this number with estimates of bulk carbon abundance of upper mantle (from 53 to 72 ppmw in depleted MORB source to >1000 ppmw in more primitive mantle [5,15,16]) would suggest that there might be regions in the upper mantle where a significant fraction, if not all of the carbon, could be accommodated by normally volatile-free silicates.

Numerous attempts to determine carbon solubility in olivine since the early 1980s [17–21] have yielded contradicting results, probably reflecting sample contamination problems. Recent data by Keppler et al. [22] suggest that normal upper mantle silicates may dissolve only traces of carbon (1–5 ppm by weight). However, a systematic study of carbon solubility in the nominally volatile-free minerals stable throughout the entire mantle remains lacking. In particular, little is known about the behavior of carbon in the transition zone and lower mantle. There are no data on carbon solubility in wadsleyite, ringwoodite, $MgSiO_3$–ilmenite and the major phase of the lower mantle, $MgSiO_3$–perovskite. Carbonates, particularly magnesite and its high-pressure polymorphs, are stable throughout most of the mantle [23–25], with diamond becoming stable in more reduced regions [26,27]. However, as $MgSiO_3$–perovskite is the most abundant mineral on Earth, even a moderate solubility of carbon would make $MgSiO_3$–perovskite in the lower mantle the largest carbon reservoir on our planet.

Here we report carbon solubility in olivine at various pressures, temperatures and redox conditions, the first precise measurements of carbon solubility in $MgAl_2O_4$ spinel, enstatite, diopside and pyrope and the first data on carbon solubility in wadsleyite, ringwoodite, $MgSiO_3$–ilmenite and $MgSiO_3$–perovskite. These data therefore cover the entire range of nominally volatile-free minerals of the Earth's mantle.

2. Experimental technique

Stoichiometric mixtures for each mineral of interest were prepared from high-purity oxides and hydroxides and were ground together with 10–20 wt.% of Na_2CO_3 certified to contain more than 99% of the ^{13}C isotope. For piston cylinder experiments, these mixtures together with about 1% of water were loaded in 10-mm-long capsules with an outer diameter of 5 mm and a wall thickness of 0.3 mm made of platinum–rhodium (95 wt.% Pt, 5 wt.% Rh), iron, cobalt or nickel. Platinum–rhodium capsules were sealed by arc welding. Iron, cobalt and nickel capsules were mechanically sealed by forcing a tightly fitting lid into the capsule. In multi-anvil runs, we used platinum capsules (1–3.5 mm long, 1–2 mm in diameter) made from 0.1-mm-thick foil.

Experiments at 1.5 GPa pressure and 900–1100 °C were carried out in a non-end-loaded Johannes-type [28] piston cylinder (PC) apparatus. Assemblies (22 mm diameter, 45 mm long) consisted of NaCl, Pyrex glass, crushable alumina, pyrophyllite and graphite. A tapered graphite heater was used to minimize thermal gradient [29]. Temperatures were measured by a NiCr–Ni (K type) thermocouple which physically contacted the sample capsule. Pressures reported include a 10% friction correction. Pressures and temperatures are estimated to be accurate to ±0.1 GPa and ±25 °C. Oxygen fugacity was not strictly controlled in runs with PtRh capsules, but the reaction of traces of water with the graphite heater results in an oxygen fugacity close to Ni–NiO buffer. The oxidation of the Fe, Co and Ni capsules in experiments Ol-11F1, Ol-11C and Ol-11N produced oxygen fugacities corresponding to the Fe–FeO (iron–wüstite), Co–CoO, and Ni–NiO buffers, respectively.

Experiments performed at 6–26 GPa and 900–1400 °C employed 500- and 1000-tonne multi-anvil presses using 32-mm Toshiba tungsten carbide cubes, pyrophyllite gaskets and 18/11 (octahedral edge length/truncation edge length), 14/8, 10/5, 10/4, and 8/3 octahedral sample assemblies made from partially sintered, Cr-doped MgO (95% MgO+5% Cr_2O_3). A $LaCrO_3$ heater (with stepped design in the 18/11 and 14/8 assemblies to reduce temperature gradients [30]) was separated from the octahedron by a ZrO_2 sleeve and from the capsule by a MgO sleeve. The capsule was positioned near the middle of the assembly by crushable alumina or MgO spacers. A W3Re97–W25Re75 thermocouple was

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