THE SOLUBILITY AND DIFFUSIVITY OF CARBON IN OLIVINE: IMPLICATIONS FOR CARBON IN THE EARTH'S UPPER MANTLE

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Abundant evidence exists for the presence of carbon in the earth's upper mantle. The amount of C, the C-bearing phases extant and their distribution, and the effect of trace quantities of C on the physical properties of the mantle remain largely known. Voluminous CO2 emissions from volcanoes (Barnes et al., 1978) and mid-ocean ridge basalts (Pineau and Javoy, 1983) bear mantle C isotopic signatures and thus indicate a present-day mantle C source. CO_2 inclusions in xenolith minerals (Roedder, 1965) are interpreted as CO_2 evolved from the magma during transport to the surface. Diamonds and graphite in kimberlite and peridotite xenoliths are further proof of C in the mantle, although radiometric ages on diamond inclusions > 3 Ga (Richardson et al., 1984) argue against these minerals as the present-day C source. The paucity of carbonate in mantle xenoliths contrasts with phase equilibrium studies indicating that carbonates, and not CO_2 , should be stable in a peridotite mineralogy (Newton and Sharp, 1975; Eggler et al., 1979). Intrinsic oxygen fugacity measurements on mantle minerals indicate that the mantle is generally not reducing enough to stabilize CH₄ (Sato, 1984). Mathez et al. (1984) analyzed 15-100 ppm C in mantle peridotites from kimberlites and alkali basalts which they interpreted as CO_2 inclusions and condensed C on grain boundaries and cracks.

Olivine in some harzburgite and lherzolite nodules from South Africa contains abundant co-precipitates of a fluid phase and spinel (Green and Guegen, 1983). The volume fraction of bubbles (<0.1 μ) corresponds to a few hundred ppm CO₂, assuming the fluid is CO₂ and has a specific gravity of 1. The bubble precipitates contain an amorphous surface film and electron energy loss spectroscopy showed C associated with the sub-grain boundaries containing these bubbles (H.W.G. and P.J. Vaughan, unpublished data). Infrared spectroscopy (IR) on these crystals and fracture of the crystals under water indicate that these bubbles are now empty (R. Borch and H.W.G., unpublished data); IR did show some water-related species (Mackwell et al., 1985; Miller and Rossman, 1985) corresponding to a few pm hydrogen. These observations indicate that the volatile species originally dissolved in the crystals contained C, and perhaps H. The decrease in the solubility of these species with decreasing pressure presumably led to the precipitation of fluid during ascent.

Freund and coworkers (Freund et al., 1980: Oberheuser et al, 1983; Knobel and Freund, 1986) claim C exists in solid solution in olivine from the mantle and further that the C species is highly mobile at low temperatures ($\langle 800 \ ^{\circ}$ K). In contrast, Mathez et al. (1986) also have analyzed C in mantle olivines using the same nuclear reaction technique as Oberheuser et al. (1983) and Knobel and Freund (1986) and find no C.

To pursue the significance of C dissolution in olivine, we have initiated an experimental program in which single crystals of San Carlos olivine are sealed in platinum capsules with 14 C-labelled silver oxalate (CO₂) and oxalic acid (CO₂-H₂O). The specimens are then annealed at 0.1 GPa in an internally heated gas apparatus or at 3.0 GPa in a solid medium apparatus at temperatures from 1200-1600 °C. Carbon concentrations are determined by the beta track method (Tingle, 1986; Mysen and Seitz, 1975). After 100 hrs. at 1175 °C and 0.1 GPa, no C was observed in crystals exposed to either CO₂ or CO₂-H₂O, indicating that at low pressure, the solubility or the diffusivity of C in olivine is very low. At 3.0 GPa, the inferred solubility from experiments on coarse-grained powders using CO₂-H₂O is 100-150 wt. ppm C independent of temperature within experimental error. At 3.0 GPa and 1200 °C, C concentration gradients extending from the surfaces into the interiors of single crystals exposed to CO₂-H₂O for 2 and 14 days yield diffusivities of 10 $^{-8}$ -10⁻⁹ mm²/sec. A single crystal exposed to pure CO₂ for 2 days at 1200 °C and 3.0 GPa the incorporation of C into the crystals or that the presence of elemental C is required for diffusion of C into the crystals (elemental C in the CO₂-H₂O experiments is

thought to be a consequence of hydrogen diffusion between the BN sample assembly and the capsule contents).

These experiments on C solubility and diffusion in olivine are consistent with observations on natural rocks in several respects. 1) Solubilities greater than 100 wt. ppm C are in rough agreement with deductions from mantle xenoliths (Green and Guegen, 1983) . 2) The apparent insolubility of C in olivine at low pressure confirms the pressure dependence of the solubility (Green and Guegen, 1983). 3) High diffusivities of C and H in olivine predict that analyses of mantle-derived olivines will underestimate their concentrations in the mantle. Condensed C on grain boundaries and cracks (e.g. Mathez et al., 1984) may represent C dissolved in the crystals that exsolved during diapiric uprise in the mantle and eruption. 4) The significant solubility of both C and H in olivine establishes that the nominally volatile-free silicates of the mantle potentially constitute a large reservoir for fluids. This would explain the origin of present-day C associated with volcanism and resolve the paradox that the absence of carbonate in mantle xenoliths presents without excluding the possibility that carbonate minerals may exist in the mantle.

C diffusivities of $10^{-9} \text{ mm}^2/\text{sec}$ are similar to Fe-Mg interdiffusivities in olivine at 1200 °C reported by Buening and Buseck (1973). These diffusivities are rapid in their geologic context, but they contrast with the high mobilities attributed to solute C by Knobel and Freund (1986) who claim C can diffuse from the bulk to the surface of olivine crystals even at room temperature. Crystals of San Carlos olivine have been exposed to a thin film of 1^4 C-bearing graphite (vapor-deposited) for two years at room temperature. If natural olivine contains C and this C species has a high mobility, as Oberheuser et al. (1983) and Knobel and Freund (1986) claim, then 1^4 C atoms at the surface should mix spontaneously with "solute" C atoms producing 1^4 C

¹⁴C atoms at the surface should mix spontaneously with "solute" C atoms producing ¹⁴C profiles into the crystals. Our failure to observe such profiles indicates that C is not mobile at room temperature and pressure in olivine.

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