CARBON IN OLIVINE BY NUCLEAR REACTION ANALYSIS

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INTRODUCTION

The possibility that C and H may dissolve in greater than trace amounts in silicates that are nominally volatile-free has important consequences for mantle petrology and mechanics. If, for example, silicates are important reservoirs for C and H, then the stabilities of fluids, graphite, diamond and other volatile-rich phases would depend on the modal mineralogy of the mantle and solubilities of the volatile elements in its constituent phases. In fact, a significant solubility for C in olivine and other minerals has been proposed in a series of papers by F. Freund and coworkers (1,2,3,4,5). In these studies it is argued (1) that C becomes concentrated in near-surface regions of olivine and other materials, reaching concentrations of greater than 2 at.% within about 5000 Å of the crystal surfaces and on the order of $10^3 - 10^4$ ppm 1-2 microns below the surface; (2) that these high surface concentrations result from the rapid diffusion of C from the crystal interiors; and (3) that C is present in a truly dissolved state, existing "atomically" (i.e., in the ground state) in both extrinsic cation vacancies and interstitial sites.

These assertions have been disputed in two recent studies. First, Mathez et al. (6) were unable to detect significant concentrations of C in one of two mantle olivine crystals using the same nuclear reaction analysis (NRA) technique employed in the Freund studies. The second crystal was found to contain C, but it was interpreted to represent C in inclusions or cracks rather than in solution. Second, Tsong et al. (7), in a study of the behavior of C on mineral surfaces, attributed the supposed diffusion properties of C to surface contamination. As a consequence of this disagreement, a more detailed study of C solubility in olivine using NRA has been conducted.

NUCLEAR REACTION ANALYSIS

The importance of NRA is that it can be used for in situ microanalysis of trace quantities of certain light elements in solid targets and that for some of these elements distinction can be made between their surface and bulk concentrations. A beam of light ions from an accelerator can be used to create nuclear reactions involving target atoms if the beam energies are sufficient to overcome the coulomb barriers of the nuclei. Nuclear reactions are customarily expressed in a shorthand form such that j(k,x)y describes a reaction in which j is the target nucleus, k the incident particle, x the reaction produce and y the residual nucleus. Useful analytical reactions include ${}^{12}C(d,p){}^{13}C$, ${}^{16}O(d,\alpha){}^{14}N$, ${}^{19}F(p,\alpha){}^{16}O$, ${}^{11}B(p,\alpha){}^{8}Be$ and ${}^{2}H(d,p){}^{3}H$, where d, p and α indicate a deuteron, proton and alpha particle, respectively. The analytical rationale is that energies of the emitted particles are "characteristic" for specific incident particle energies and that their intensities are proportional to concentrations.

For d-p reactions, the proton spectrum also provides information on the concentration of target nuclei as a function of depth (Fig. 1). The concentration of C in the bulk target is represented by the integrated signal (shaded), excluding that from the surface. In the case of olivine, the bulk signal originates from 2000 Å to 3 microns below the surface. The distinction between surface and bulk concentrations is particularly important in the case of C because most materials readily adsorb C from the atmosphere, and thus their surfaces are severely contaminated.

The experiments were conducted using the Van de Graaff accelerator at Los Alamos National Laboratory. A 1.3 MeV deuteron beam was focused with a superconducting magnet. Although beam diameters of < 20 microns can be achieved, thermal and radiation damage of the olivine limited the minimum beam size to 125 microns. The energy resolution of the entire system is 20 KeV, which corresponds to a depth resolution

(Fig. 1) of \sim 1700 Å in olivine. This means that C concentrations can be determined in individual layers 1700 Å thick and 125 microns wide.

A major problem of the NRA technique for C analysis is that there is a significant interference in the C proton spectrum from d-p reactions involving Mg and Si. For a typical mantle olivine, Mg and Si account for backgrounds that are equivalent to 700 and 100 ppm at. C, respectively. These important background components contribute significantly to the magnitude of the detection limit, which for olivine is computed at 65 ppm at. from consideration of counting statistics only. An important requirement of the technique is that the analytical surface must be flat over the region of the beam. For rough surfaces, the proton signal from surface C is smeared to lower energies and thus yields an apparent bulk C signal. Some previous studies may have suffered from an incomplete knowledge of the background and problems associated with surface roughness. As a check on accuracy and analytical procedure, a C-bearing diopside glass was analyzed (Fig. 2A). Analysis by NRA indicated a C content of 2.4 at.%, which compares with a concentration of 2.2 % obtained by electron probe. A typical olivine spectrum is shown in Fig. 2B.

RESULTS

Olivine crystals from four different geological environments but of similar compositions (Fog0-92) were studied. None of the samples were found to contain C in detectable quantities, i.e., in concentrations > 65 ppm at. (= 37 ppm wt.). The samples include: (a) Four gem-quality crystals from Zabargad Island (Red Sea), Egypt. Fluid inclusions indicate that they crystallized under shallow crustal conditions in the presence of hypersaline fluid (8). (b) Crystals separated from Group 1 spinel lherzolite xenoliths and mantle-derived megacrysts from alkali basalts from the southwest USA. They are believed to have recrystallized in the presence of CO2-dominated fluids at pressures of 6-8 kb. (c) Two San Carlos megacrysts, one of which was held in contact with graphite and the other with magnesite at 30 kb and 1400°C for 24 hours. The samples were prepared by Trace Tingle as part of a separate study on C solubility. The regions analyzed include those within 100 microns of the contacts between the olivines and C-rich phases. (d) Olivines from two granular garnet lherzolite xenoliths from the Finsch kimberlite pipe, RSA. One of the xenoliths contains diamond, and compositions of coexisting phases from it and other Finsch lherzolites indicate equilibration conditions of > 50 kb and \sim 1130°C (9).

It is concluded that the solubility of C in olivine is negligible under all conditions found in the crust and upper mantle and that analytical problems likely plagued some of the earlier experiments to the extent that their reliability is questionable.

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Figure 1. (a) Illustration of the ${}^{12}C(d,p){}^{13}C$ nuclear reaction technique. Deuterons of initial energy $E_d{}^0$ lose energy as they penetrate the target, acquiring energies of E_{d1} , E_{d2} , and E_{d3} at depths of 1, 2, and 3 microns. Protons produced at corresponding depths have initial energies such that $E_{p1}{}^0 > E_{p2}{}^0 > E_{p3}{}^0$. The proton energies are dependent on deuteron energies at specific depths and the energy inherently released by the nuclear reaction. Protons lose energy as they escape from the target and at the detector possess energies $E_{p0} = E_{p0}{}^0 > E_{p1} > E_{p2} > E_{p3}$. (b) An idealized proton spectrum from a target containing C in its bulk. Note the correspondence of channel number, proton energy and depth. The complex shape of the spectrum is partly due to the variation with depth of nuclear cross sections of target atoms for deuterons. Modified from ref. (5) and (6).



Figure 2. Particle spectra of (a) diopside + CO_2 glass and (b) Zabargad olivine (Fog2). The glass contains 2.2 at. % C. Carbon in the olivine spectrum is atmospheric contamination and within 1000-1400Å of the surface. Most of the background above channel 614 is due to Mg, with a small contribution from Si.