

OXYGEN IN DIAMOND BY THE NUCLEAR MICROPROBE: ANALYTICAL TECHNIQUE AND INITIAL RESULTS.

(1) J.D. Blacic; (2) E.A. Mathez; (3) C. Maggiore; (3) T.E. Mitchell and (2) R. Fogel.

(1) Geophysics Group, Earth and Space Sciences Division, Los Alamos National Laboratory, Los Alamos NM 87545

USA; (2) Department of Mineral Sciences, American Museum of Natural History, New York, NY 10024, USA;

(3) Center for Materials Sciences, Los Alamos National Laboratory, Los Alamos, NM 87545 USA.

Investigations of diamonds indicate that oxygen, along with light volatile elements, is a major impurity in diamond (Sellschop, 1979), suggesting that the oxygen content of diamond may be used to qualitatively characterize the oxidation state of its source region. This is of interest because some diamonds contain reduced mineral inclusions such as moissanite (SiC) and iron metal (e.g., Moore and Gurney, 1989; Meyer and McCallum, 1986), implying that some parts of the upper mantle are reduced and that its oxidation state is variable.

The analysis of oxygen in diamond has been accomplished by an *in situ* microactivation technique. Diamonds were bombarded with a 4.5 MeV beam of ^3He ions. The beam was focused to a spot 200-300 μm across with a superconducting solenoid, which provided for relatively high beam currents and short activation times (1.5-2 hrs.). The analytical depth extends to $\approx 8 \mu\text{m}$. The incident ions interact with carbon and oxygen in the diamonds according to the reactions $^{12}\text{C}(^3\text{He},\alpha)^{11}\text{C}$ and $^{16}\text{O}(^3\text{He},p)^{18}\text{F}$. Both reaction products are radioactive and decay by positron emission. However, because the half lives of ^{11}C and ^{18}F are 20.9 and 109.7 minutes, respectively, their decay activities, which are determined by coincidence counting with NaI detectors, are easily distinguished on a plot of decay activity vs. time (Fig. 1). The theoretical detection limit of the technique is <10 ppm atomic oxygen, but in practice it is limited by the amount of oxygen adsorbed on the diamond surface. The precision, which is limited by precision in measurement of the ^3He beam current, is $\approx 15\%$ relative.

Two problems are associated with the analytical surface. The first involves adsorbed atmospheric oxygen and arises because there is no facility in the sample chamber to remove (e.g., by sputtering) the adsorbed layer. The amount of oxygen adsorbed on nominally clean, polished diamond surfaces exposed to atmosphere was determined by Rutherford backscattering spectrometry (RBS). Surface oxygen concentrations are typically $\approx 1 \times 10^{15}$ at/cm² (detection limit $\approx 0.4 \times 10^{15}$ at/cm²), in agreement with previous estimates (Sellschop, 1979). This amount, representing ≈ 15 ppm in the bulk analysis, is equivalent to a continuous monolayer of surface oxygen and, since diamond surfaces are not known to oxidize, is taken to be the maximum amount that can be adsorbed. A more serious problem is due to the build-up of an oxygen-rich contaminant on the analytical surface during activation. Elimination of this contamination, which is apparently due to a sealant in the sample chamber, was necessary because it adds significant oxygen to the analysis. The ^{18}F nuclei produced by reaction (2) possess an energy of 2.2 MeV; thus most ^{18}F generated in the contaminant is implanted in the diamond and cannot be removed.

The problem was circumvented by coating nominally clean diamonds before activation with a 2 μm thick layer of gold, which serves to trap the ^{18}F from the contaminant. The configuration is illustrated in Fig. 2. After activation and before counting, the gold coat and trapped contaminants were removed by polishing. After the diamonds were counted, their surfaces were reexamined by RBS to confirm that all gold had been removed.

We examined nine type IIA (verified by IR) and five type I diamonds. The former are doubly polished 1 mm plates purchased commercially. Oxygen contents were found to range from 16 to 102 ppm at. (ave. = 67 ppm). The type I diamonds are fragments each with a single polished face. Their oxygen contents range from 49 to 116 ppm (ave. = 81 ppm). The ranges are similar to those reported by Bibby and Sellschop (1974) determined by fast neutron activation.

There are several potential sources of oxygen. One possibility is that oxygen exists in the gold coats and the analyses are artifacts. However, there is no indication that the gold layers contain oxygen, and the variability in the analyses cannot obviously be accounted for by this possibility. Experiments are presently underway to confirm this. A second possibility is that oxygen is contained in inclusions. Although the regions analyzed in all samples are free of inclusions or other defects visible by optical microscopy, submicroscopic inclusions are possible. To test this, two type IIA diamonds were examined by TEM and were found to be inclusion free. Type IIA diamonds are known to possess relatively high concentrations of dislocations, so a third possibility is that oxygen exists in such structures. The average dislocation density, which was determined by counting the number of intersections with the diamond surface, was found to be $\approx 2 \times 10^{13}/\text{m}^2$. Only ≈ 1 ppm oxygen can be accommodated in dislocations assuming that their cores are undissociated and saturated with an oxygen atom at every atomic position along the dislocation. If the dislocation cores are dissociation in saturated stacking faults 40 \AA wide, concentrations as high as 10 ppm are possible. However, higher concentrations must be in solution.

References Cited

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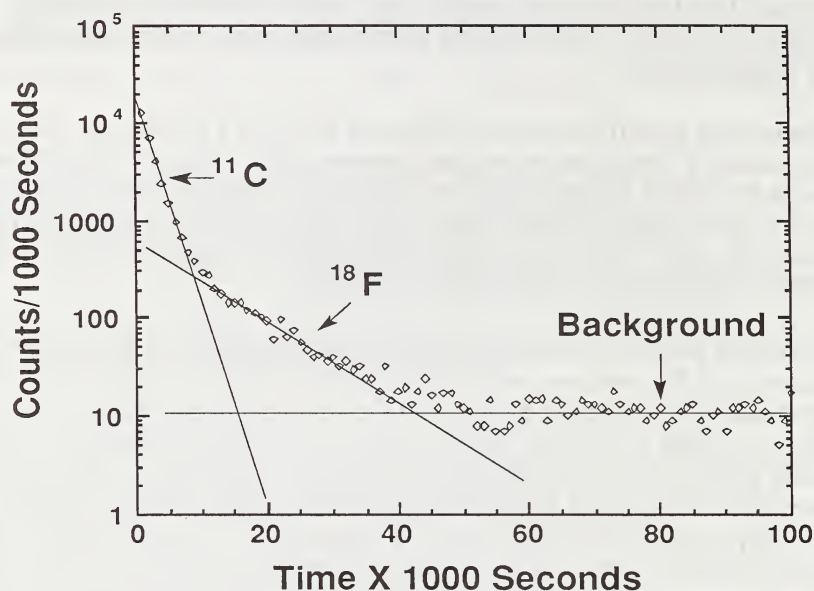


Fig. 1. Decay activity of diamonds activated by ^3He . The activity is composed of three components representing decay of ^{11}C ($t_{1/2} = 20.9$ min.), ^{18}F ($t_{1/2} = 109.7$ min.) and a background, which is constant with time.

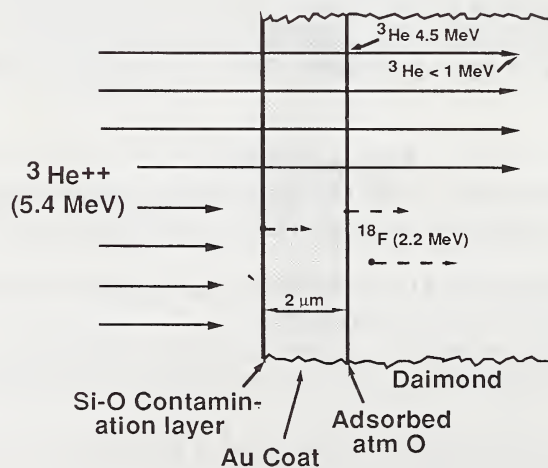


Fig. 2. Configuration of a gold coated diamond being activated by ^3He . ^{18}F is generated from a layer of contamination on the gold, from the diamond surface (which had been exposed previously to the atmosphere), and from within the diamond itself.