

Natural and laboratory α -particle irradiation of diamond

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SUMMARY. To produce a lattice expansion readily detectable by conventional X-ray photographic means in α -irradiated diamond, a dose of order 10^{18} α .cm⁻² is required. Such a dose could be produced by pitchblende in $\sim 2 \times 10^8$ yr. and a previously reported lattice expansion in a natural diamond could therefore have occurred by long-term contact with a radioactive material. α -particle doses greater than $\sim 10^{14}$ cm⁻² produce observable green colouration on the surface of an initially colourless diamond.

FAST-NEUTRON irradiation gives rise to an expansion of the diamond lattice (Primak *et al.*, 1956; Keating, 1963, 1968). Since a lattice expansion can be produced in silicon by both fast-neutron (Baldwin, 1968) and α -irradiation (Burgeat and Colella, 1969), it would be expected that α -particle irradiation of diamond would produce a lattice expansion.

Meyer *et al.* (1965) studied diamonds from Precambrian deposits of the Ivory Coast, Africa, that had dark green patches on their surfaces. X-ray measurements on fragments, consisting of clear diamond with a green skin, showed evidence of a lattice parameter expansion of about 0.3 %, which was confined to the skin. The skin thickness was ~ 20 μ , about the range of a 5 MeV α -particle in diamond. Natural radioactive minerals emit α -particles with energies of ~ 5 MeV, neglecting self-absorption. Meyer *et al.* (1965) concluded that the green patches were formed by α -emitting minerals being in contact with the diamond surface for long periods of time.

Diamonds showing green patches, similar to those found in the Ivory Coast, have now been found in each of many diamond deposits and are common in some (Milledge, to be published).

The aim of the present work was to find whether a lattice expansion could be produced in diamond by laboratory α -irradiation, the α -dose required, and thus whether the expansion effects observed in the Ivory Coast diamonds could in fact arise from natural α -irradiation.

Experimental

X-ray measurements were made photographically using Cu radiation and a 3 cm radius camera. The X-ray specimens were normally small fragments, < 0.5 mm in

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size. As an α -particle source, ^{210}Po in both solid and aqueous form was used in the early part of the work but to obtain significantly higher α -doses a linear ion accelerator (IBIS; AERE, Harwell) was used, which provided 3 MeV He^+ ions. The solid ^{210}Po source consisted of a very thin circular layer, 7 mm in diameter, which was covered by a thin aluminium window. The initial activity was 2.2 Ci.cm^{-2} and the α -energy, after passing through the window at normal incidence, was 4.9 MeV. The aqueous ^{210}Po source consisted of 0.5 cm^3 of a solution of 1.0 Ci.cm^{-3} initial activity.

Results and discussion

Ivory Coast and Venezuelan diamonds. Milledge *et al.* (1965) found that heating in air to $\sim 600^\circ\text{C}$ caused the green patches on the Ivory Coast diamond (Meyer *et al.*, 1965) to turn to a brownish colour but that the lattice expansion persisted.

In the present work, the fragments used by Milledge *et al.* (1965) were heated in vacuum at 1050°C for 1 hr, which removed the expansion effects. No further colour changes ensued. The effect of heating on the expansion is in general accord with annealing results on neutron-irradiated diamonds that had undergone a density decrease of a few per cent (Primak *et al.*, 1956; Vance, 1971). Several diamonds with green patches on their surfaces from the Precambrian deposits of Venezuela were broken up but only fragments containing the very darkest patches of skin showed any evidence ($\leq 0.2\%$) of an expansion detectable by X-ray rotation photographs. However, since various pieces of the green skin all turned brownish after heating above $\sim 600^\circ\text{C}$ in vacuum, the colour change obtained by Milledge *et al.* (1965) would not appear to be due to the action of air on the heated specimens.

α -irradiation. Colourless West African diamonds were exposed to the solid and liquid ^{210}Po sources for 66 days (the half-life of ^{210}Po is 138 days), the doses being calculated as $2 \times 10^{17} \alpha.\text{cm}^{-2}$ and $\sim 10^{14} \alpha.\text{cm}^{-2}$ ($3 \leq E \leq 5.3 \text{ MeV}$) respectively. The relatively small dose from the aqueous source was due to absorption of the α -particles by the water. The diamond exposed to the aqueous source turned a very pale green, reminiscent of the even green colouration observed on many diamonds from the Finsch Mine in South Africa. However, this result does not prove that the green colour of Finsch diamonds has been caused by α -radiation; more work is required to draw any conclusions on this point. The diamonds exposed to the solid source turned a very dark green. Some were broken up, and X-ray rotation photographs were obtained from fragments containing $>10\%$ of the irradiated skin. No fragments however showed a lattice expansion though, as before, heating above $\sim 600^\circ\text{C}$ in vacuum turned the green skin to the characteristic brownish colour.

Colourless diamond flats from the Premier mine (Africa) were glued with vinyl acetate to a water-cooled target and subjected to a dose of $2.5 \times 10^{19} \alpha.\text{cm}^{-2}$ at a current density of $60 \mu\text{A.cm}^{-2}$. The irradiated surfaces of the diamonds were rendered black. Small pieces, $\sim 20 \mu$ thick, of the irradiated skin were readily removed from the diamonds. A density measurement, using diluted Clerici's solution, on the largest fragment, gave the fractional density decrease due to irradiation as 21%, in agreement with that deduced from X-ray photographs of the fragments; virtually no Laue

spots were observed on stationary-crystal photographs and only diffuse 111, 220, and 331 spots on rotation photographs (see Vance, 1971). There would, therefore, be a very large strain between the damaged and undamaged portions of the diamond; it is not surprising that the parts of the damaged layer were readily removed from the bulk of the diamond. A completely colourless surface was left. If such heavy doses had occurred naturally, it is quite likely that the skin would subsequently become disengaged from the diamond; the remaining diamond would not be recognized as having suffered irradiation.

For diamonds, of various shapes, irradiated to rather lower doses using the linear accelerator α -source, the (black) skin could not be removed from the diamonds. The irradiated diamonds were therefore broken up and X-ray rotation photographs were obtained from several fragments containing $> 10\%$ of skin. Using a current density of $60 \mu\text{A.cm}^{-2}$, a dose of $4.0 \times 10^{18} \alpha.\text{cm}^{-2}$ produced a lattice parameter expansion of 1.1% , as evidenced on rotation photographs by 'extra' diffraction maxima on the low-angle side of the maxima due to the unexpanded diamond substrate. The 'extra' maxima were fairly sharp (see also Burgeat and Colella, 1969). At the same current density, a dose of $1.3 \times 10^{18} \alpha.\text{cm}^{-2}$ produced no observable expansion (the experimental limit of accuracy was about 0.15%). However at a current density of $30 \mu\text{A.cm}^{-2}$, a dose of $1.3 \times 10^{18} \alpha.\text{cm}^{-2}$ produced a lattice parameter expansion of 0.6% . This result is readily explained since there was evidence that, at the current density of $60 \mu\text{A.cm}^{-2}$, the mean temperature of the diamond was in excess of 200°C ; due to annealing processes, the higher the specimen temperature at which irradiation is carried out, the less the expansion produced by a given dose.

Vacuum annealing experiments on a fragment of a diamond subjected to $4.0 \times 10^{18} \alpha.\text{cm}^{-2}$ showed that 70% of the original expansion remained after a treatment of 1 hr at 650°C , but that none of the original expansion could be detected after annealing above 900°C . These results substantially agree with the above-mentioned annealing data on the Ivory Coast fragments.

Since specimen heating was negligible in the irradiation with the solid ^{210}Po source, and no lattice expansion was detected with the dose of $2 \times 10^{17} \alpha.\text{cm}^{-2}$, it is concluded that the lattice expansion in the Ivory Coast diamond was produced by a dose in excess of $2 \times 10^{17} \alpha.\text{cm}^{-2}$. Since $1.3 \times 10^{18} \alpha.\text{cm}^{-2}$ at a current density of $30 \mu\text{A.cm}^{-2}$ produced an observable lattice expansion, it is concluded that the Ivory Coast diamond received approximately $10^{18} \alpha.\text{cm}^{-2}$, if the irradiation took place at about room temperature. If, however, the irradiation took place at a higher temperature, the dosage would have to be correspondingly greater. It should be noted, however, that irradiation must have taken place at temperatures below $\sim 600^\circ\text{C}$, otherwise the patches on the surface of the Ivory Coast diamonds would have been brown, not green. The question now arises as to whether a dose of $10^{18} \alpha.\text{cm}^{-2}$ could be produced by a natural radioactive source. Because of its high uranium content, pitchblende would be a likely candidate. There will be a thickness λ_c , of pitchblende such that α -particles traversing a distance λ_c before impinging on the diamond will not have sufficient energy to cause appreciable displacement damage. Taking λ_c as 5 to 10μ it is readily calculated that $10^{18} \alpha.\text{cm}^{-2}$ would be produced on the surface of a diamond

in direct contact with pitchblende in $\sim 2 \times 10^8$ yr. For diamonds from Precambrian deposits, this is a plausible figure. For radioactive sources less rich in uranium, the time to produce a dose of $\sim 10^{18} \alpha.\text{cm}^{-2}$ would be correspondingly longer.

By suitable refinement of the X-ray technique, it should be possible to detect a lattice expansion in diamonds subjected to considerably less than $10^{18} \alpha.\text{cm}^{-2}$. Another promising line of approach would be to study surface patterns obtained by etching diamonds, in which α -irradiation is suspected, in molten KNO_3 ; Mendelsohn (1971) has obtained considerable evidence that radiation damage produces an accelerated etch rate in diamond.

However, it must be noted that a quantitative knowledge of the α -dose received by a diamond does not allow a time of exposure to the radioactive material to be deduced, because the diamond and the (unknown) radioactive mineral in question will not be recovered together in the mining process. We hope, however, to obtain minerals such as olivine in direct contact with uranium-bearing minerals to see whether the α -dose received by the olivine (for instance) correlates directly with the age of the uranium-bearing minerals. Preliminary experiments with 3 MeV He^+ ions show that a dose of $2 \times 10^{17} \alpha.\text{cm}^{-2}$, at the low current density of $2.6 \mu\text{A}.\text{cm}^{-2}$ produces considerable darkening of the surfaces of olivine, garnet, and diopside (the only minerals we have studied so far).

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