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Differences among low Ceylon zircons

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SUMMARY. Low Ceylon zircons showing an optical absorption band at 5200 Å appear to have suffered more radiation damage than other low Ceylon zircons. Very heavy fission-fragment irradiation failed to lower the density of each of two low Ceylon zircons significantly, although the specimens were rendered completely amorphous. Further fission-fragment irradiation experiments indicated that low Ceylon zircons showing a previously reported anomalous absorption spectrum have been heated late in their geological histories.

ZIRCON is prone to radiation damage from α-particles emanating from uranium or thorium impurities (see e.g. Blumenthal, 1958; Deer *et al.*, 1962). Depending on the amount of lattice disordering, which depends mainly on the concentration of radioactive atoms and the geological age of a specimen, a zircon may be classified as high (relatively undamaged), intermediate, or low (heavily damaged) (Anderson, 1941). Anderson (1962, 1963) has observed differences in the optical absorption spectra of low Ceylon zircons having densities near 4·00 $\mathrm{gm.cm^{-3}}$ and refractive indices near 1·80. The majority of low zircons showed only a weak diffuse optical absorption band near 6560 Å. A very small minority showed an anomalous (A) spectrum. An even smaller minority were similar to the majority class but showed an additional band at 5200 Å. These three types will now be referred to as X, Y, and Z respectively.

Anderson (1962) found that Y-type material could be produced by heating X- or Z-type material to 800 to 1000 °C. Vance and Anderson (1972) found that an X-type stone could not be converted to a Z-type stone by heating at temperatures lower than those required to convert it to a Y-type stone.

It was suggested in Vance and Anderson (1972) that Y-type material may have suffered more radiation damage than X-type material, though the simplest explanation would be that after reaching the X-state, the material had been heated sufficiently to convert it to the Y-state. It was found that, whereas the one X-type and three Y-type stones studied showed weak Laue spots on stationary crystal X-ray photographs, of two Z-type stones studied one showed no Laue spots and the other showed a near-absence of Laue spots.

It is the purpose of the present work to report further experiments undertaken to try to understand the above differences among low Ceylon zircons.

Experimental

Optical absorption, density, and refractive index measurements were made as described by Anderson (1962, 1963). X-ray work was carried out as described in Vance and Anderson (1972). Fragments, weighing ~1 mg., of some stones were neutron-irradiated in the DIDO reactor at AERE, Harwell. The Analytical Research and Development Unit at AERE, Harwell performed neutron activation analyses for U and Th on samples weighing ~50 mg. Annealing treatments were carried out by heating in air.

The properties of the zircons used for the experiments herein described are given by Vance and Anderson (1972; this vol., p. 605), except for *Z*2; this 1·906 g. specimen had density 4·01 g.cm^{-3}, *n* 1·823, and a strong 5200 Å band; only one out of six X-ray photographs showed any trace of Laue spots.

Results and discussion

5200 Å band. The results on stone *Z*2 confirmed the correlation of the 5200 Å band with the absence or near-absence of Laue spots on stationary crystal photographs (see above), suggesting that the *Z*-type stones have suffered more radiation damage than stones *X* and *Y*. X-ray photographs of fragments of stone *Z* and *Z*1, after annealing at 1150 °C, showed powder patterns indexing as tetragonal ZrO_2, similar to results reported in Vance and Anderson (1972) for stones *X* and *Y*. However, whereas high-temperature annealing (~1300 °C) restored *X* and *Y* to slightly imperfect single-crystal zircon, similar high-temperature annealing of fragments of *Z* and *Z*1 caused reversion to polycrystalline zircon, though some fragments showed vestiges of preferred orientation. These results support the view that *Z*-type stones have suffered more radiation damage than stones *X* and *Y*.

Since increasing radiation damage lowers the density of zircon, it would be expected that *Z*-type stones would have lower densities than stones *X* and *Y*. This was not the case. Small fragments of stones *X* and *Y* were neutron-irradiated to a total dose of 6×10^{19} nvt (fast)+4×10^{20} nvt (slow). This fast neutron dose caused the density of several diamonds to decrease by $3{\cdot}8\pm 0{\cdot}3$ % (a recent description of the X-ray behaviour of neutron-irradiated diamonds has been given by Vance, 1971). However, the main damage mechanism for metamict zircon, containing U, is the slow-neutron fission of ^{235}U (further damage will also arise from fast-neutron fission of ^{238}U and slow neutron fission of ^{239}Pu, produced from ^{238}U). Although the fission cross-sections are not large, 160 MeV of kinetic energy, shared between the fission pair, is liberated in each fission event (see Wittels, 1959; Wittels *et al.*, 1962). To calculate the number of fission events, the U content of stones *X* and *Y* was found by neutron activation analysis. The results were 5500 and 5700 ppm by weight respectively. These values agree with values calculated from the data of Holland and Gottfried (1955) and are not far short of the highest recorded (to our knowledge) U contents in Ceylon zircon (6400 ppm, Gottfried *et al.*, 1956; 6200 ppm, Vaz and Senftle, 1971). The calculated number of fission events was $1{\cdot}2\times 10^{17}$ cm^{-3}, the main contribution being the fission of ^{235}U. The calculated burn-up of ^{235}U was 25 %. Because of induced radioactivity, nearly six months had to be allowed to elapse before X-ray and density measurements were made. The densities of the irradiated fragments of *X* and *Y* were each measured as $3{\cdot}96 \pm 0{\cdot}02$ gm.cm^{-3} by suspension in diluted Clerici's solution and it seems reasonable that this value represents the approximate lower limit of the density of a Ceylon zircon. X-ray stationary crystal photographs showed the irradiated fragments of both stones to be entirely amorphous, with no trace of Laue spots. After annealing at 850 to 1000 °C X-ray photographs showed the diffuse powder pattern indexable as cubic ZrO_2; after annealing at 1150 °C, photographs showed a sharp powder pattern, which indexed as tetragonal ZrO_2. The irradiated material therefore had the X-ray characteristics of *Z*-type low Ceylon zircon, in agreement with the theory that *Z*-type material has suffered more radiation damage than stones *X* and *Y*.

TABLE I. *Irradiation responses of X- and Y-type material*

Slow neutron dose, nvt.	X-ray stationary crystal photographs of fragments of stones *X* and *Y*	
	X†	*Y*
—	Weak Laue spots	Weak Laue spots, plus diffuse powder pattern indexable as cubic ZrO_2.
5×10^{17}	,,	,,
4×10^{18}	No Laue spots, *very* faint powder lines not indexable as ZrO_2.	,,
2×10^{19}	Amorphous	Very faint Laue spots, very weak powder pattern indexable as cubic ZrO_2.
8×10^{19}	Amorphous	Amorphous

† A fragment of *X* annealed for 1 hr at 850 °C gave the same responses as *Y*.

X → Y transformation. The possibility of transforming *X*-type material to *Y*-type material by irradiation was mentioned above. The U content of stone *Y* was slightly greater than that of stone *X* (the Th contents of *X* and *Y* were measured as 125 and 28 ppm by weight respectively, showing the Th/U ratio to be very small, as concluded by Gottfried *et al.* (1956)). Hence if the geological ages and the thermal histories of *X* and *Y* were the same, and the lattice breakdown independent of the original crystal quality, stone *Y* would have suffered slightly more radiation damage than stone *X*. There is considerable evidence that all Ceylon zircons have an age of 570×10^6 yr, within experimental error (Tilton and Aldrich, 1955; Gottfried *et al.*, 1956). Holland and Gottfried (1955) found a good correspondence between the α-dose and the densities of Ceylon zircons. However diamonds, heavily irradiated with fast neutrons, showed considerable discrepancies in densities and X-ray behaviour even when from the same batch (Vance, 1971); it would seem that the quality of the original crystal may affect the degree of lattice breakdown produced by a given dose of neutrons (or α-particles). The irradiation responses of fragments of *X* and *Y*, together with fragments of *X* annealed 1 hr at 850 °C to transform them to *Y*-type material before irradiation are shown in Table I.

Although the mechanisms of fission fragment and α-irradiation are different, there is no compelling reason to believe that fundamentally different results should obtain when a near-amorphous solid is bombarded with massive particles, even though the energies involved are different; this is supported in the present instance by the observation that the end-product appears to be amorphous whether fission fragments or α-particles are employed. Hence it would seem that *X*- and *Y*-type material have different irradiation responses and that *Y*-type material does not represent a state of greater radiation damage than *X*-type material. It is therefore concluded that *Y*-type material has been heated late in its geological history, after reaching the *X*-state (see above).

In view of the excellent correlation found in Vance and Anderson (1972) between the A spectrum and X-ray powder pattern indexable as cubic ZrO_2, a possible explanation of the observation that some edges of stone *Z* showed the diffuse powder pattern indexable as cubic ZrO_2, but that the stone did not show the A spectrum, is that the edges in question were subjected to local heating during cutting or polishing or both.

Conclusions

Z-type material has suffered more radiation damage than *X*-type material, though intermediate material presumably exists. The lower limit of the density of low Ceylon zircons must be about 3·96 $gm.cm^{-3}$. *Y*-type material is apparently only produced by heating *X* or *Z*-type material.

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