X-RAY INVESTIGATION OF ZIRCON CRYSTALS
CONTAINING OH GROUPS

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Substitution of $(OH)_4$ for SiO_4 in certain zircons and thorites has been indicated by Frondel (1953) and in thorogummite and coffinite by Stieff *et al.* (1956). Collett and Frondel (1957) have synthesized zircon and
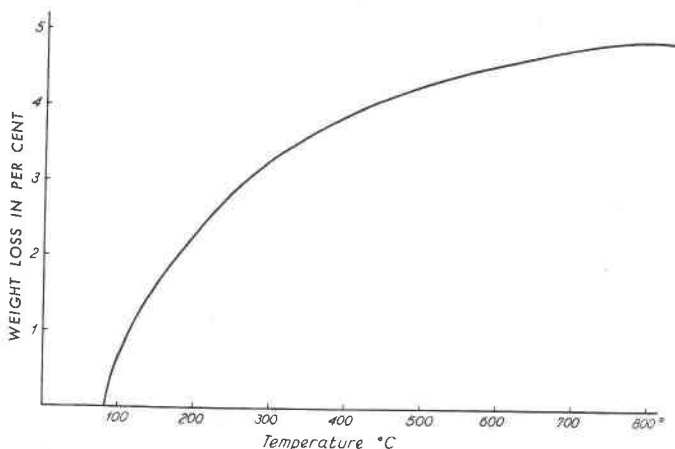

Fig. 1. Dehydration curve.

thorite and, from the results of infra-red absorption spectra, concluded that this material contained (OH) groups; however, Mumpton and Roy (1961) in their experiments found no evidence in support of this substitution.

In the course of an extensive study of granitic pegmatites in Yugoslavia, M. Ristić and S. Pavlović found in a pegmatite from Prokuplje area, Serbia, zircon crystals associated with beryl, albite, muscovite and quartz. Subsequent investigations revealed the presence of 1.09% uranium and 0.09% thorium (determined by γ-radiometry) and a certain amount of water. Powder and single crystal photographs showed a certain degree of metamictization.

All of the investigation has been carried out with one group of zircon crystals ranging in size from 1 to 10 mm. Some of them had well developed faces, and the presence of the following forms was established: (010), (110), (011), (121) and (112). Water was determined on a Chevenard

thermobalance, and the curve obtained is given in Fig. 1. It is very similar to the dehydration curve obtained by Kostiljeva (1946) from completely metamict zircons from Karelia. From the shape of our curve it is difficult to determine the amount of water present as OH groups in the structure, although more than 1% loss in weight is above 400° C. Infrared measurements were made on a Perkin-Elmer spectrophotometer with a rock salt prism, using Nujol oil as a mounting medium (Fig. 2). In the region between 2 and 7 microns there is one absorption band at 2.97 microns and a weak absorption band at 6 microns. All these absorptions remained unchanged after the specimens were heated at 200° C. for 10 hours. On the basis of the above results we have assumed that the part
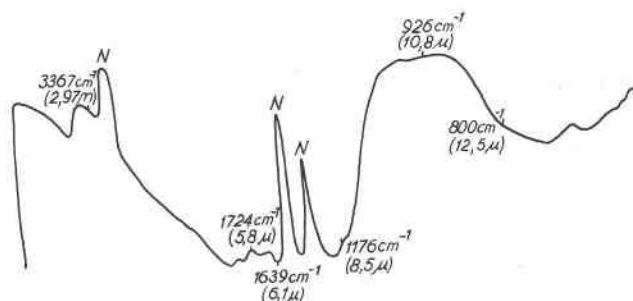

FIG. 2. Infra-red absorption curve: absorptions due to the mounting medium (Nujol) are indicated by the letter N.

of the water present is held in the structure in the way it was suggested by Frondel.

Unit cell dimensions have been determined on the Weissenberg goniometer using CuKα radiation. A cylinder, 0.2 mm in diameter, was ground from a larger crystal and was coated with NaCl powder for the purpose of calibration. The following results were obtained:

$$a = 6.622 \pm 0.002 \text{ Å}$$
$$c = 6.024 \pm 0.002 \text{ Å}$$

These values indicate a slight increase in unit cell dimensions compared with those in "normal" zircon (Krstanović, 1958). We were unable, within the limits of experimental error, to detect anisotropic expansion of the a_1 and a_2 axes (Ueda, 1957).

Data about the behavior of bond distances and angles in radiation damaged structures are rare. Since it was possible to measure the intensities of the reflexions of these zircons up to $\sin \theta / \lambda = 1.0$, with Mo radiation, we have decided to redetermine the oxygen positions for comparison with those in "normal" zircon. For that purpose 64 0kl and 30 hk0 reflexions

were recorded on an integrating Weissenberg goniometer. Intensities were measured with a photometer and, after allowing for Lorentz and polarization factors and for absorption, F values were placed on absolute scale by scaling them to the calculated structure amplitudes. To calculate the structure amplitudes atomic parameters from the structure of "normal" zircon were used (Krstanović, 1958); the atomic scattering factors were taken from the Internationale Tabellen (1935).

Oxygen positions have been refined by F_0 and $F_0 - F_c$ syntheses, and the following parameters for oxygen atoms were obtained: $x = 0.064$, $z = 0.201$; the value for reliability index was 0.09. Interatomic distances in the structure are as follows:

$$O\text{-}O = 2.47 \text{ Å (two)}, \quad O\text{-}O = 2.73 \text{ Å (four)}, \quad Si\text{-}O = 1.62 \text{ Å},$$
$$Zr\text{-}O = 2.13 \text{ Å (four)}, \quad Zr\text{-}O = 2.33 \text{ Å (four)},$$

with $\rho(x)$ estimated to be 0.03 Å (Cruickshank, 1949). However, a component with the scattering power of about one fourth of the oxygen was detected on F_0 and $F_0 - F_c$ maps, the coordinates of the peak being $x = 0.11$ and $z = 0.20$. Taking into account the geometry of the zircon structure and after comparing electron densities maps of two zircons (*i.e.* "normal" zircon and the one under present investigation) we conclude that this peak originated from the rupture of Zr-O bonds during metamictization, followed by a slight shift in the orientation of SiO_4 tetrahedra. This must lower the symmetry of the structure as a whole, and we have found that all sections cut perpendicular to four-fold axes show a 2V of about 4°. Further refinement of this structure as well as a refinement of oxygen positions in zircons of various degrees of metamictization is in progress in order to obtain a better understanding of the process of metamictization of this mineral.

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