

The water content of a synthetic quartz

W. C. GODBEER AND R. W. T. WILKINS

CSIRO Division of Mineralogy, North Ryde, N. S. W., Australia

Abstract

New water determinations are reported on X_0 , a synthetic quartz which has been widely used for deformation studies. The infrared (0.059 wt.% H_2O) and classical ($0.046 \pm .002$ wt.% H_2O) values are lower than that recently reported using the IBSCA technique by a factor of about 50.

Since Griggs and Blacic (1965) first reported the experimental plastic deformation of synthetic quartz, it has been clear that the deformation behavior of quartz is strongly influenced by its 'water' content. Until recently, infrared determinations of water in quartz, calibrated by electrolytic exchange experiments of Brunner *et al.* (1961) or by the theoretical study of Kats (1962), have been widely accepted, largely because better techniques were not available. As Kats' discussion shows, infrared determinations may not be of high accuracy for several reasons, but chiefly because it is difficult to allow for changes in the molar extinction coefficient with band frequency in complex OH spectra. The contribution made by each distinctive form of water, information of vital significance in correlating deformation studies and which can only be obtained by infrared analysis, is also poorly known.

With the application of IBSCA (Ion Beam Spectrochemical Analyzer) to the problem (Tsong *et al.* 1976), values have been reported which are one to two orders of magnitude above those previously available for the same specimens. There is a residual possibility that some hydrogen may be present in a form which is not observable in the OH vibrational spectrum. At the suggestion of Drs. Tsong, McLaren, and Hobbs, we undertook to review the infrared data and to perform a careful classical water determination on X_0 , the original crystal of Griggs and Blacic.

X_0 has a simple spectrum (Griggs and Blacic, 1965; Griggs, 1967; Blacic, 1975) consisting of a single broad band in the hydroxyl stretching region. There are no sharp bands such as have been attributed to OH ions associated with a variety of point defects (Kats, 1962; Dodd and Frazer, 1965). The broad

band may be assigned to the vibrations of water in gel-like regions (Bambauer *et al.*, 1969). Kirby (1975) has shown that, after deforming X_0 at about 500°C, the OH spectrum is modified to the typical band shape of liquid water and with almost the same intensity. This is caused by the precipitation of structural water into submicroscopic fluid inclusions (McLaren and Retchford, 1969). We may overcome calibration problems with little error, therefore, by using the well-established molar extinction coefficient for liquid water, ϵ (20°C) = $55 \text{ mole}^{-1} \text{ l cm}^{-1}$ (Fox and Martin, 1940), to determine the water content of the quartz. On a (10 $\bar{1}0$) plate using unpolarized radiation a value of 0.0066 percent H or 0.059 percent H_2O , corresponding to 3940 H/10 6 Si, was obtained. This compares well with the revised value (4350 H/10 6 Si) given by Brunner's method (Blacic, 1975).

A Gallenkamp twin tube furnace was used for the conventional water determination. The sample in an alumina boat is moved into the hot zone of the mul-lite tube furnace by a magnetic push rod while dry oxygen from a common source is passed simultaneously through both tubes at a controlled flow rate. Under these conditions, hydrogen in all forms should be converted to water. The water evolved during a period of exactly 25 minutes is collected on magnesium perchlorate contained in glass U-tubes. The samples were crushed in a percussion mortar and sieved to <400 μm diameter. They were neither ground nor acid-washed, as these treatments were found to appreciably increase the measured water content. Lithium metaborate was employed as flux to fuse the quartz and ensure liberation of all water. Microscopic examination of the glassy residue showed that with a flux to sample ratio of 1.5:1,

quartz fuses completely in a normal run at 1250°C. Lithium metaborate was ignited at 750°C, but still yielded a blank of ~ 1.5 mg water which, added to the blank inherent in the system, gave a total blank of ~ 2.5 mg. This fluctuated slightly throughout the day, but was shown not to differ between tubes when run at the same time by more than 0.02 mg. One tube was therefore used to monitor the blank while the sample was run at the same time and under the same conditions in the other. A determination of water in a Canadian standard reference rock MRG-1 (Abbey *et al.*, 1975) gave a figure of 1.03 percent H₂O+ against a recommended value of 1.02 percent H₂O+. Two separate runs on 0.5 g samples of X₀ quartz at 1250°C and 1400°C yielded 0.24 and 0.22 mg H₂O, representing 0.048 and 0.044 percent H₂O+. The reported IBSCA value for this specimen is 0.23 weight percent H or 2.07 weight percent H₂O.

Considering the difficulties inherent in water determinations at this level, the agreement between infrared and conventional determinations is satisfactory. Although it appears that IBSCA will eventually be the definitive method for the determination of water in minerals, the values which it yields at present on minerals with a trace water content are too high by a factor of 10 to 100. The values reported in this paper are at the same general level as those reported for other nominally anhydrous silicates (Wilkins and Sabine, 1973).

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