

# LETTERS TO NATURE

## Hydroxyl Ion Diffusion in Quartz

THE diffusion of univalent cations through quartz was first observed in 1887 (ref. 1) and has been the subject of several investigations since<sup>2,3</sup>. But there seems to be a lack of data on the movement of anions through the quartz lattice, although these ions are present in that mineral<sup>4</sup>. The most abundant anion, which may be present in greater quantities than the total cation content, is the hydroxyl ion<sup>5</sup> which has been shown to weaken quartz by forming silanol bonds<sup>6</sup>. The formation of bubbles<sup>7</sup>, the accompanying decrease in silanol bonds and increase in free water<sup>8</sup>, in annealed quartz, indicate that the diffusion of hydroxyl ions must occur.

Hydroxyl ion diffusion was studied by applying a potential across basal sections of piezoelectric grade quartz in contact with a platinum anode and a pellet of goethite ( $\text{Fe}(\text{OH})_3$ ) as cathode. The experimental procedure was exactly that used for cations<sup>2</sup>, and the conductivity for the resultant ionic currents<sup>9</sup> increased exponentially with temperature. A plot of the log of the conductivity against the reciprocal of the temperature (K) is linear (Fig. 1) and the gradient of such a plot is dependent on the activation energy for the conduction process, in this instance the movement of hydroxyl ions. The energy values, which were determined by the least squares method on an IBM 7044 computer, varied between 10 and 13 kcalories  $\text{mol}^{-1}$  for temperatures  $400^\circ\text{C}$  to  $500^\circ\text{C}$  and an applied field of  $1,000\text{ V cm}^{-1}$ . These values increase with a decrease in the field intensity as is the case for cationic diffusion<sup>8</sup>. The extrapolated value for diffusion at zero field intensity was 15 kcalories  $\text{mol}^{-1}$ .

The quartz sections which had been used in the diffusion experiments were irradiated to reveal the areas through which ionic migration had actually occurred<sup>2</sup>. Samples from these, and from adjacent unaffected areas were analysed, qualitatively, in a Perkin-Elmer 457 infrared spectrophotometer. Hydroxyl ions, present as silanol bonds, were detected in the diffused areas but none were observed in the adjacent areas through which diffusion had not occurred (Fig. 2). Similar effects have been observed for cationic diffusion<sup>10</sup> and my experiments demonstrate that the observed currents were the result of hydroxyl ion migration. Because the anionic currents exhibited similar characteristics to those reported for cationic currents<sup>9</sup>, the diffusion mechanism in quartz must be similar for all ions.

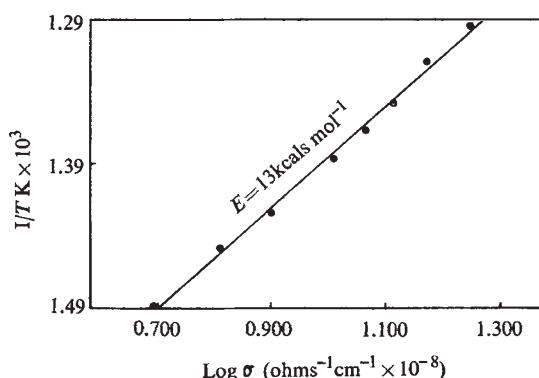


Fig. 1 A plot of the conductivity,  $\sigma$ , against the reciprocal of the temperature (K) for hydroxyl ion diffusion. The gradient of this plot gave an activation energy of 13 kcalories  $\text{mol}^{-1}$  for hydroxyl ion diffusion in quartz.

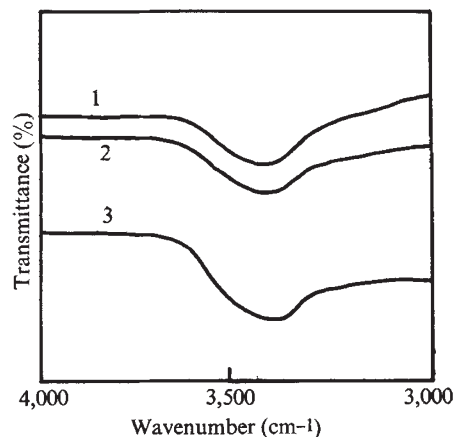


Fig. 2 Infrared traces which show the presence of silanol bonding in the quartz through which hydroxyl ion diffusion had occurred (curve 3). Curve 1 is a blank and curve 2 is the trace from the quartz areas through which hydroxyl ion diffusion had not occurred.

Hydroxyl ions should readily diffuse into quartz, as indicated by the low activation energy, during metamorphism. This would lead to the formation of silanol bonds and result in a weakened form of quartz<sup>6</sup> which would deform and recrystallize with ease<sup>11</sup>. The values of activation energies obtained for hydroxyl ion diffusion are similar to those required for the recovery of deformed water weakened quartz<sup>12</sup> and this further supports the theory that dislocation climb in quartz is dependent on the movement of hydroxyl ions.

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## Water Dynamics in Clays by Neutron Spectroscopy

THE behaviour of water near solid surfaces is of current interest<sup>1</sup> and, in particular, much attention has been paid to the water-clay interaction in layered aluminosilicates<sup>2</sup>. In