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NOTE

SEPIOLITE ANHYDRIDE AND CRYSTAL FOLDING

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The structure of sepiolite folds when crystals are heated to remove their water. This folding occurs by rotation of the structural blocks on axes through the Si–O–Si edge bonds which join the fiber units. The folded form is often spoken of as sepiolite anhydride and has been said to occur when the zeolitic water and the water coordinated to Mg at fiber edges are lost from the channels (Preisinger, 1959).

Much evidence in this laboratory by X-ray powder diffraction, thermogravimetric and i.r. spectroscopic techniques suggests that sepiolite folds to the "anhydride-like" structural form when only about half of the water of coordination is removed. The second half of the water of coordination may then be removed from the folded sepiolite at much higher temperatures, but produces almost no further structural change.

The structural model, Fig. 1, shows a section of a sepiolite crystal. The right hand side of the figure represents an external edge of the crystal. The corner groups are Si–OH (Ahlrichs *et al.*, 1974), each being hydrogen bonded (at a) to one water of coordination. These groups, produce i.r. absorption at a frequency of 3718 cm^{-1}, typical of perturbed Si–OH frequencies. The two waters of coordination, when found in internal channels of the crystal, form bridges as illustrated by b in the model and serve to stabilize the open crystal channels of the structure.

When half of the water of coordination inside of the channels is lost (below 200°C in vacuum or near 300°C in air) a structure illustrated by Fig. 2 is proposed. All the external edge water are lost and therefore part of the Si–OH (b) are free to vibrate at a higher frequency of 3738 cm^{-1} compared to its previous frequency of 3718. The rest of the Si–OH (c) produces a new frequency at 3726 cm^{-1} because it forms a weak association with the neighbouring oxygen surface. Thus, initial removal of part of the water of coordination produces two i.r. bands for Si–OH in place of the one normally present in sepiolite. Neither of these two new frequency bands is further affected by the removal of the remaining water and they only disappear by dehydroxylation at very high temperatures long after the last water is removed.

In the folded structure, magnesium ions located at the edge inside channels complete their coordination with oxygens of the neighbouring surface (g). One water molecule (d) remains coordinated to each of those magnesium ions. Its position is just above the pseudohexagonal hole of the adjacent fiber unit, thus perturbing the structural hydroxyl located inside the hole (e). I.r. evidence supports this by showing the normal 3680 cm^{-1} frequency of structural $(Mg)_3OH$ to shift about half to a new 3697 cm^{-1} frequency, and the remaining OH groups (f) to vibrate near 3680 cm^{-1} (actually 3674).

Thus, removal of about half of the water of coordination also produces a band split in the 3680 cm^{-1} band. However, removal of the remaining water should eliminate the band split in this case because it is dependent upon the perturbation by water. This is found to be true. With removal of the last water at 530°C under vacuum, the band split disappears and the complete band reappears near its original frequency of 3680 cm^{-1}.

Our model, based mainly on i.r. evidence, suggests that partially dehydrated sepiolite is a folded structure which contains nearly half of the original water of coordination trapped in hexagonal holes.

The model also suggests that removal of this remaining

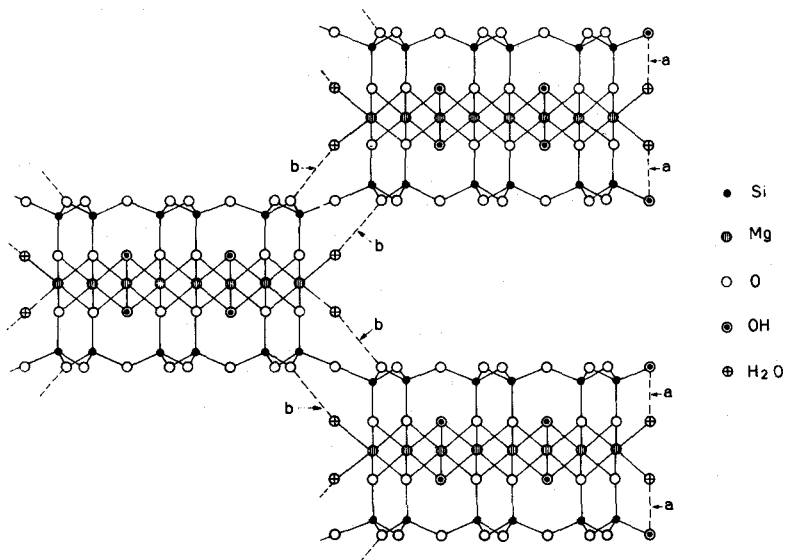


Fig. 1. End view of the edge of a model sepiolite fiber. (a) water–SiOH bond, (b) water–oxygen bond.

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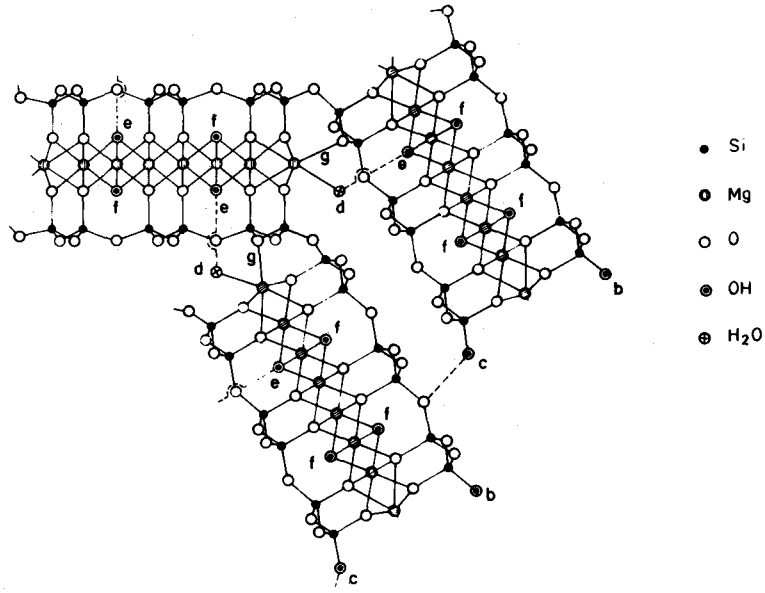


Fig. 2. End view of the edge of a model sepiolite crystal which folded after losing half of its water of coordination. (b) unperturbed Si–OH. (c) perturbed Si–OH by bond to surface oxygen. (d) remaining internal water. (e) perturbed octahedral OH. (f) unperturbed octahedral OH. (g) Mg^{2+} to oxygen bond.

water to produce the anhydride should cause little, if any, additional structural change. Thus, with heating a sepiolite anhydride-like structure is attained long before the sepiolite is a true anhydride.

Recently, Nagata *et al.* (1974) proposed the same folding mechanism based on the changes of X-ray powder diffraction patterns. Their samples were heated without vacuum and the folding occurred at 300°C.

Thermogravimetric, X-ray powder diffraction, and additional i.r. determinations afford complementary evidence for the model proposed. Complete data will be presented in a later paper.

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