

The dehydration of caoxite: the topotactic transformation to whewellite

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[Introduction]

Whewellite [Ca(C₂O₄)·H₂O], weddellite [Ca(C₂O₄)·2H₂O] and caoxite [Ca(C₂O₄)·3H₂O] are known as calcium oxalate hydrate minerals (Gaines et al., 1997; Basso et al., 1997). These crystal structures are characterized by conformation of edge-shared CaO₈-polyhedra that cements the linkage between water molecule and oxalate ion (C₂O₄²⁻). Based on the polyhedron model, caoxite, weddellite and whewellite are composed of dimers, chains and sheets respectively. There is structural speculation (Tomazic and Nancollas, 1979) that caoxite could be a precursor to weddellite and whewellite formation. It is said that the polymerization of polyhedra likely constructs the series of structures (e.g. Basso et al., 1997). The actual dehydration process of synthetic caoxite was characterized by direct transformation into whewellite at 389.5K not via weddellite (Morishige et al., 1999). Thus, in consideration of the behavior of the water molecules, it is not topologically possible for mere condensation of CaO₈-polyhedra to proceed from one structure to the next.

The present work studies the behavior of the water molecules with IR spectra of the calcium oxalate minerals and re-investigates the structural hierarchy of the calcium oxalate minerals that provides an explanation for the actual dehydration process.

[Sample and experimental]

Single crystals of whewellite from Bilina, Czech, weddellite from urinary calculi and caoxite as previously reported (Morishige et al., 1999) were obtained for this study. IR spectra were collected using a Janssen-type micro-FTIR spectrometer (JASCO corp.) in the region from 4000 to 650 cm⁻¹. Each spectrum was obtained with 1 cm⁻¹ resolution and 1000 scans at room temperature.

[Results and discussion]

The band at around 1650cm⁻¹ that attributes to C=O stretching vibration was observed in all the spectra commonly. In contrast, the O-H stretching band of whewellite and caoxite occurred at 3476 cm⁻¹, 3429 cm⁻¹ respectably, whereas that of weddellite was located at 3286 cm⁻¹. It can be inferred that the similarity of the bands between whewellite and caoxite is implied in the affinity between the geometrical environments of water molecules in the crystal structures. In addition, the O-C=O bending vibration around 780 cm⁻¹ in whewellite is similar to that in caoxite. It may be attributed to bonding-mode of the oxalate ion (C₂O₄²⁻) common in the crystal structures.

Compared with the crystal structures of whewellite, weddellite and synthetic caoxite (Tazzoli and Domeneghetti, 1980; Deganello et al., 1981), oxalic groups alternate with calcium ions, and both of them construct the ribbons common in whewellite and caoxite, although the structural feature is not contained by weddellite. In addition, adjacent ribbons are bound together by independent oxalate ions to form sheets. The water molecules of caoxite appear to be intercalated to fold sheets by the hydrogen bonding. With increasing temperature and dehydration, i.e., with decreasing hydrogen bonding, ribbon-oxalate sheets are flattened and oxalate ions combining ribbons would form bonds with calcium ions included in opposite sheets, constructing the whewellite structure.