

Synchrotron powder X-ray diffraction study of the structure and dehydration behavior of sepiolite and palygorskite

Jeffrey E. Post¹ and Peter J. Heaney²

¹ Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560-0119, U.S.A.

² Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

Real-time, temperature-resolved synchrotron powder X-ray diffraction data and Rietveld refinements provide unprecedented insights into mineral behaviors and mechanisms of crystal structure transformations. As examples, we will discuss investigations into the behaviors of the sepiolite structure from 300 to 925 K and the monoclinic palygorskite structure from 300 to 1400 K. Sepiolite and palygorskite are hydrous Mg,Al-rich silicate clay minerals with fibrous morphology that typically occur as fine-grained, poorly crystalline masses. They occur in a wide variety of geological environments and have been mined for centuries because of their many useful properties. Sepiolite and palygorskite boast more than 100 commercial uses today in the pharmaceutical, fertilizer, and pesticide industries, and their versatile functionality derives from the large surface area and microporosity that are characteristic of the materials. Because of their fine-grained and poorly crystalline natures, it has not been possible to study the crystal structures of sepiolite and palygorskite using single-crystal diffraction methods, and consequently many details of the structures are not well known. In this study we used temperature-resolved real-time synchrotron X-ray powder diffraction and Rietveld refinements to investigate in unprecedented detail changes in the sepiolite and monoclinic palygorskite structures as they dehydrated and collapsed from 300 to 1100 K. Results of a series of refinements of the “anhydrous” sepiolite structure over the temperature range ~ 666 to 925 K confirmed both the basic folded-structure model for “anhydrous” sepiolite and the existence of two “anhydrous” phases.

The RT palygorskite structure revealed that the Al atoms are ordered into the inner M2 octahedral sites and the Mg cations into the M3 sites at the edges of the tunnels. The refinements using temperature-resolved data revealed that most of the zeolitic H₂O is lost from the palygorskite structure in air by ~ 425 K, and the crystallographically bound H₂O is lost in two stages, at temperature intervals of 475-540 K and 580-725 K. Above ~825 K a portion of the sample transformed to a folded structure.