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Crystal structures of two partially dehydrated chlorites: The "modified" chlorite structure

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ABSTRACT

Chromian clinochlore-*IIb*-4 (triclinic) and *IIb*-2 (monoclinic) polytypes from the Day Book Body, North Carolina, were heated to 650 °C for 5 hours and air quenched. Single-crystal X-ray refinements of the (metastable) product phases resulted in $R = wR = 0.056$ and $R = wR = 0.061$ for the triclinic and monoclinic forms, respectively. The heat-treated triclinic form has $C\bar{1}$ symmetry and cell parameters $a = 5.368(1)$, $b = 9.297(2)$, $c = 14.215(6)$ Å, $\alpha = 89.86(3)$, $\beta = 97.15(3)$, $\gamma = 89.98(2)°$, and $V = 703.95(36)$ Å^3, and the monoclinic form has $a = 5.372(1)$, $b = 9.291(2)$, $c = 14.270(7)$ Å, $\beta = 97.34(3)°$, and $V = 706.4(4)$ Å^3 in $C2/m$ symmetry. The product structures are topotactic with the parent phases, with the 2:1 layer of the product nearly identical to that of the parent. Dehydroxylation of the interlayer of the parent produces two quasi-planar sets of atoms between adjacent 2:1 layers. Although, based on the refinement of the average structure, the cations and anions are apparently disordered in these planes, cations (Mg, Al, Cr) must have three oxygen atom nearest neighbors and oxygen atoms must be coordinated to three cations. Apparent disorder is related to lateral displacements of the interlayer planes within the (001) plane. Interlayer-site to interlayer-site distances are near 1.8 Å. Second nearest-neighbor distances for most of the interlayer sites are short, near 2.3 Å. A model is proposed where, at high temperatures, the interlayer planes become more extended and planar, but the planes "crumple" upon cooling to more closely approach higher-order nearest-neighbor atoms. These changes upon cooling might be a significant driving force for additional cation and anion ordering in the interlayer, since the interlayer sites have very different second nearest-neighbor environments. Thus, with appropriate cooling rates, cation ordering possibly may be obtained. However, the development of an ordered pattern of cations and anions may also be dependent on kinetics; decomposition is favored over time because of the instability of threefold-coordinated interlayer ions.