The Dehydroxylation of Chlorite and the Formation of Topotactic Product Phases

Wudi Zhan and Stephen Guggenheim

Department of Geological Sciences, University of Illinois at Chicago 845 W. Taylor St., Chicago, Illinois 60607-7059

Abstract: Single-crystal, X-ray examination of Mg,Fe-rich chlorites that were heated at 650° C for 24 hours in air and have undergone dehydroxylation of the interlayer shows that two product phases result with a topotactic relationship, with the *c* axis of both phases parallel. One phase ("modified chlorite" or "14-A phase") has relatively sharp reflections with a 14-A *c*-axis repeat, indicating that it is well crystallized and maintains the 2:1 layer from the parent. Cell parameters are a = 5.368(1)A, b = 9.297(2)A, c = 14.215(6)A, $a = 89.86(3)^{\circ}$, $\beta = 97.15(3)^{\circ}$, $\gamma = 89.98(2)^{\circ}$, and it crystallizes in Cl_{\Box} symmetry. A structure refinement, details of which will be reported later, indicates that the interlayer consists of two planes, each containing (M + O), where M is the interlayer cation species. These planes show about $\pm 0.5A$ positional disorder along the [001] direction. There is no evidence for scattering material at z = 0.5 between the 2:1 layers. The second phase in the topotactic relationship is based on a 27-A unit *c* axis ("27-A phase"). The diffraction data are limited with about 15 diffuse reflections observed, indicating that it is poorly crystallized. The 27-A spacing suggests that both octahedral sheets in the parent chlorite contribute to the formation of this phase.

Heating Mg,Fe-rich chlorite powder in a closed system to 550° C, under either reducing or oxidizing conditions, prevents the formation of the 27-A phase. Because the 27-A phase forms in an open system, we infer that water fugacity is an important factor in its formation. Heating experiments involving samples with different polytypes and octahedral " type" (dioctahedral *vs* trioctahedral) of the 2:1 layer suggests that these two variables are important. However, the results are equivocal, and an ill-defined B-rich chlorite from Madagascar breaks the observed trends for both variations in stacking sequence and octahedral type. However, B-content may be a factor in the transformation also for those chlorites that contain B.

Key Words: Chlorite • Dehydroxylation • Topotactic phases • X-ray diffraction

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