

New insight into the structural transformation of partially dehydroxylated pyrophyllite

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ABSTRACT

Two pyrophyllite samples, one S037, from the Coromandel region of New Zealand and the other, S076, from Berosovska, Ural, Russia, were studied by thermogravimetric (TG and DTG), infrared (IR), and X-ray diffraction (XRD) methods to investigate structural transformations of these samples at different stages of their partial dehydroxylation. The samples were heated at different temperatures during 45 min and the degree of dehydroxylation was estimated as a ratio of mass loss of each particular heated specimen to the total mass loss of the sample during total dehydroxylation.

Sample S076 consists only of *trans*-vacant (*tv*) layers because its DTG curve and IR spectrum contain a single dehydroxylation maximum at $T_{\max} = 723$ °C and an OH stretching band 3675 cm^{-1} , respectively. In sample S037 *tv* and *cis*-vacant (*cv*) layers are interstratified at random and its DTG and IR spectrum contain, respectively, two dehydroxylation maxima at 595 and 760 °C and two stretching bands at 3675 and 3668 cm^{-1} . The positions and intensities of the reflections in the experimental powder XRD patterns of sample S037, as well as the refined parameters of the unit cell, almost coincide with those determined for 1A pyrophyllite. However, the XRD patterns contain an “additional” peak with $d = 4.454(6)$ Å, which is absent in normal 1A pyrophyllite. This peak can be considered as an indicator of a structure in which *tv* and *cv* layers are interstratified.

The XRD patterns from the oriented specimens of the studied samples heated above 500 °C show splitting of the basal reflections. Simulation of the XRD patterns from oriented specimens of the S076 sample show that the phase composition of the specimens is the same independent of the heating temperature and represents a physical mixture of a non-treated original pyrophyllite and an almost completely dehydroxylated phase, which contains 5% of non-dehydroxylated layers. The higher the temperature, the higher the content of the dehydroxylated-rich phase in the heated sample.

Simulation of the XRD patterns from the heated S037 samples show that the phase composition of each specimen is a physical mixture of low- and high-dehydroxylation phases, referred to as LD and HD phases, respectively. Each of these phases is a mixed-layered structure in which the original non-dehydroxylated (ND) and completely dehydroxylated (CD) layers are interstratified at random. The main difference between these phases is that in the LD phase the content of ND layers prevail, whereas in the HD phase CD layers dominate. The increase in temperature and degree of dehydroxylation change the relative content of the LD and HD phases as well as the relative amount of ND and CD layers in these phases.

Interstratification of ND and CD layers in the LD and HD phases is not consistent with the commonly accepted model according to which during dehydroxylation of pyrophyllite and related layer silicates, non-dehydroxylated and dehydroxylated domains can coexist within one layer. As a result of this inconsistency, the model explaining the wide temperature interval of pyrophyllite dehydroxylation needs to be reconsidered. A similar inconsistency arises with the model predicting the formation of several intermediate semi-dehydroxylated structures during pyrophyllite dehydroxylation because evidence for such phases was not observed.

A new model of pyrophyllite dehydroxylation is presented, which is consistent with the hypothesis, that the reaction is homogeneous and spontaneous nucleation and growth of completely dehydroxylated layers takes place during pyrophyllite dehydroxylation. In terms of this model, the large temperature interval of pyrophyllite dehydroxylation is related to particle size distribution as well as to structural disorder. A mechanism for the formation of the mixed-layered structures of the LD and HD phases is proposed.

Keywords: Pyrophyllite, dehydroxylation, modeling, structural features, FTIR, DTG, XRD