Pressure-induced transformations in kaolinite

MARK D.WELCH1,* AND WILSON A. CRICHTON2,3

1The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.
2The European Synchrotron Radiation Facility, Rue Jules Horowitz, 38043 Grenoble, Cedex 9, France
3Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, U.K.

ABSTRACT

The compressional behavior of kaolinite (space group C1) from Keokuk, Iowa, has been studied to 7.8 GPa under static compression by synchrotron X-ray powder diffraction. Two phase transformations occur at ~3.7 (kaolinite-I/II) and ~7 GPa (kaolinite-II/III) that are registered by major changes in diffraction patterns. The layer shift involved in the I/II transformation preserves hydrogen-bonded contacts across the interlayer. This transformation removes cross-interlayer Al-Si superpositions and is analogous to the low-/high-dickite transformation, which occurs at ~2.6 GPa (Dera et al. 2003). The 7 GPa transformation from kaolinite-II to “kaolinite-III” involves considerable contraction of the a-b plane (2.5%), marked shortening normal to the polyhedral layers, and a volume contraction of about 3%. Comparison of experimental patterns of kaolinite-III with those calculated for non-standard polytypes predicted by ab initio methods to 60 GPa by Mercier and Le Page (2009) allows the identification of kaolinite-III with their high-pressure, one-layer Model 18 polytype. Kaolinite-III can be quenched to room pressure, although significant transformation to kaolinite-I was observed at 0.5 GPa on decompression. At ambient conditions kaolinite-III is 6% more dense than kaolinite-I, nacrite, and low-dickite. Elastic moduli for kaolinite-I and kaolinite-III have been obtained that indicate that kaolinite-III is more compressible than kaolinite-I, due primarily to in-plane (a-b) softening. Both high-pressure polytypes encountered experimentally were predicted ab initio to be strong candidates for high-pressure structures by Mercier and Le Page (2008, 2009). This agreement between experimental and ab initio studies is encouraging for the application of ab initio methods to complex polytypic systems.

Keywords: Kaolinite, high pressure, transformations, polytypism

INTRODUCTION

The kaolin-group minerals kaolinite, dickite, and nacrite are of considerable geological, industrial, and technological importance. These minerals are di-octahedral 1:1 phyllosilicates. While many studies of the thermal behavior and geochemistry of kaolin-group minerals have been made, their structural behavior in response to pressure is largely unstudied. Dera et al. (2003) found that dickite (space group monoclinic Cc) undergoes a reversible isosymmetric polytypic transformation to a high-pressure structure “high-dickite” at ~2.6 GPa. The transformation involves the removal of Al-Si superpositions across the interlayer (i.e., normal to the polyhedral sheets) and the formation of bifurcated hydrogen bonds.

Mercier and Le Page (2008) reported the results from an ab initio study of polytype stability in kaolin-group phases for all 20 distinct standard structures with one-layer repeats and 16 distinct two-layer structures derived by stacking alternately the two one-layer enantiomorphs. They identified polytypes that on compression (ab initio) have significantly lower enthalpies than kaolinite, the most stable zero-pressure phase, and are candidates for possible high-pressure structures. Although the transformation pressures obtained ab initio are approximate, “due to slight imperfections in the atomic potentials used in all the DFT programs” (Mercier and Le Page 2008), some interesting indicators of relative stability were proposed and likely high-pressure polytypic transformations suggested.

Mercier and Le Page (2009) extended their ab initio studies of kaolin-group structures to 60 GPa and found that two similar high-pressure phases (their models 3 and 18) were substantially more stable than any of the low-pressure polytypes (Mercier and Le Page 2008) and also than any of the other 17 new high-pressure polytypes. These two high-pressure structures (Mercier and Le Page 2009; Table 2; Fig. 4) are non-standard polytypes because the layer shifts involved lead to hydrogen-bonding topologies and interlayer connectivities that are different from those of the standard low-pressure polytypes. Here we report the structural behavior of kaolinite from Keokuk, Iowa, studied under static compression to 8 GPa by synchrotron X-ray powder diffraction, and we compare our results with the predictions of ab initio modeling.

EXPERIMENTAL METHODS

A sample of kaolinite (space group C1) from Keokuk, Iowa, was used. This locality is noted for producing exceptionally well-crystallized kaolinite with little stacking disorder. The high quality of Keokuk kaolinite was confirmed in the present study in which 020, 110, T11, T13, 01T1, and 111 reflections were found to be sharp and well resolved.

X-ray diffraction experiments were carried out on station ID27 at the European Synchrotron Radiation Facility, Grenoble, France. The powder sample and a ruby for pressure calibration were loaded into a membrane-driven diamond-anvil cell fitted with 600 µm diamond culets and a T301 steel gasket with a 250 µm hole drilled by spark-erosion. A 4:1 by volume methanol/ethanol mixture was used as the pressure medium. Pressures were measured on-line using a laser. Ruby R1 and R2 peaks were fitted with Lorentzian lineshapes and the pressure determined from the R1

* E-mail: mdw@nhm.ac.uk