The effects of grinding on the structure of a low-defect kaolinite

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ABSTRACT

Numerous studies have demonstrated the presence of at least two distinct kaolinites in individual kaolinite samples, one a low-defect material and the other a moderate- to high-defect material. Other studies have shown that some kaolinites contain the lowest-defect material in the coarsest size fractions whereas others contain the lowest-defect kaolinite in the finest fractions. In an attempt to clarify possible mechanisms for producing such kaolinite samples, we have used powder X-ray diffraction to study the effects of mechanical grinding on the nature of layer stacking in the >40 μm fraction of the American Petroleum Institute kaolinite standard no. 9 from Mesa Alta, New Mexico. This material is relatively rich in a low-defect kaolinite. Hand grinding for 10 min plus grinding under acetone for up to an additional 34 min in an automatic agate grinder produced significant changes in its diffraction pattern. However, further dry grinding in a ball mill for 10 min produced material that was almost totally disordered, based on measures such as the Hinkley index. The diffraction patterns of the wet-ground materials showed evidence of increasing disorder that could be modeled best as a physical mixture of low- and high-defect material, consistent with a physical mixture of the original ordered phase with varying amounts of a highly disordered material. Disorder in the high-defect kaolinite is caused by the interstratification of normal kaolinite layers with their enantiomorphs. Contrary to expectations, grinding of kaolinite does not produce a progressive increase in disorder for all of the crystallites present in a sample. Instead, grinding apparently creates increased amounts of a disordered kaolinite that coexist with relatively unaffected material. There is no evidence for the occurrence of an intermediate disordered phase. Contrary to previous reports, disorder caused by physical stress does not include random layer displacements of ±b/3.

INTRODUCTION

The nature of disorder in kaolinite has been the subject of scrutiny for over 50 years yet unanswered questions remain. For example, do natural disordered samples crystallize in a disordered state or have they been disordered by physical action? Might we expect kaolinite that crystallized with a disordered stacking sequence to be distinct from one that has suffered from natural physical action? Clearly, some kaolinites crystallize with a partially disordered stacking sequence, e.g., the common vermicular kaolinite books that are typically disordered (see Murray et al. 1993; Galan et al. 1996). Indeed, our own work has shown that large, macroscopic kaolinite crystals are typically quite disordered.

Numerous authors have shown that natural kaolins often consist of mixtures of kaolin minerals (e.g., Keller and Haenni 1978). In addition, detailed diffraction studies have shown that many individual kaolin samples consist of mixtures of at least two distinct kaolinites, one a low-defect material and the other(s) a moderate- to high-defect material (Plançon et al. 1989). During size separations of a variety of kaolinite samples, Bish and Chipera (1998) discovered that the diffraction patterns of a particular sample varied greatly depending on the particle size fraction analyzed. They found that the smallest fraction of the API no. 9 kaolinite contained the most disordered kaolinite, whereas the largest fraction of KGa-1 contained the most disordered kaolinite. Furthermore, analysis of the X-ray diffraction (XRD) data for each size fraction using the expert system of Plançon and Zacharie (1990) suggested that all fractions of KGa-1 and API no. 9 consisted of at least two kaolinites. The very different relationship between disorder and size fraction in KGa-1 and API no. 9 emphasized their remarkable dissimilarity and suggested the possibility of a genetic relationship.

Brindley and Robinson proposed in 1946 that disorder in kaolinite was caused by randomly distributed layer shifts of ±b/3 along the Y direction. Their model was consistent with experimental data showing relatively unaffected k = 3n reflections (e.g., 20l, 13l) and deterioration of the k ≠ 3n reflections (e.g., 02l, 11l) in diffraction patterns of disordered kaolinites. Later, theoretical considerations suggested that such translations were energetically unfavorable (Giese 1982), and experimental and theoretical work led to the presently accepted and rather complicated model of kaolinite disorder (Plançon and Tchoubar 1977; Bookin et al. 1989; Plançon and Zacharie 1990). This model includes three types of defects: defects in the placement of the vacant octahedral site; two possible translation directions between layers of approximately –a/3 and –a/3 + b/3; and modification of these interlayer translations by random shifts. It is noteworthy, in particular, that those defects in the