In situ atomic force microscopy study of hectorite and nontronite dissolution: Implications for phyllosilicate edge surface structures and dissolution mechanisms

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ABSTRACT

The dissolution behavior of two smectite minerals, hectorite (tremohedral) and nontronite (dioctahedral), was observed in situ, in acid solutions, using atomic force microscopy. As expected, the crystallites dissolved inward from the edges, and the basal surfaces appeared to be unreactive during the timescale of the experiments. The hectorite (010) faces appeared to dissolve about 6× more slowly than the lath ends, usually broken edges. The edges visibly dissolved on all sides, and appeared to roughen somewhat. On the other hand, the (010), (110), and (110) faces on nontronite crystals were exceptionally stable, so that any dissolution fronts originating at broken edges or defects would quickly become pinned along these faces, after which no more dissolution was observable. These observations can be explained by using periodic bond chain theory to predict the topology of the surface functional groups on the edge faces of these minerals. If a certain amount of predicted surface relaxation is allowed on the (110) and (110) faces of nontronite, an important difference between the exceptionally stable faces and the others becomes apparent. That is, the oxygen sites connecting the octahedral and tetrahedral sheets are all fully bonded on the nontronite (010), (110), and (110) edge faces, whereas all hectorite edge faces and nontronite broken edges would have coordinatively unsaturated connecting O atoms. This explanation for the differential reactivity of these crystal faces implies that the rate limiting step of the dissolution process is the breaking of bonds to connecting O atoms.

INTRODUCTION

Atomic Force Microscopy (AFM) is a powerful tool to explore various aspects of the structure, microtopography, and surface reactivity of minerals (see Nagy and Blum 1994; Hochella 1995; Hochella et al. 1998). Perhaps its greatest strength, from a geochemical perspective, has been the ability to make quantitative measurements of changing surface microtopography in situ, as minerals react in aqueous solutions (Drake et al. 1989; Hillner et al. 1992; Dove and Hochella 1993; Bosbach and Rammensee 1994; Dove and Chermak 1994; Junta and Hochella 1994; Bosbach et al. 1995; Putnis et al. 1995; Bosbach and Hochella 1996; Bosbach et al. 1996, 1998; Grantham and Dove 1996; Liang et al. 1996; Junta-Rosso et al. 1997; Teng et al. 1998; Rupe and Hochella 1999). Such observations often reveal that some mineral faces are more reactive than others, and given a model of the crystallographic structure of these faces, one can sometimes infer the dominant mechanism(s) of the surface reaction in question (e.g., Liang et al. 1996; Bosbach et al. 1998; Rupe and Hochella 1999).

Due to the extreme anisotropy of their structures, phyllosilicate surfaces have been shown to exhibit strong differential reactivity (Schofield and Samson 1953; White and Zelazny 1988; Anderson and Sposito 1991; Zachara and McKinley 1993; Bleam 1993; Turpault and Trotignon 1994; Brady et al. 1996). However, until recently the applicability of in situ AFM techniques to phyllosilicate surface reactivity has been limited due to two major factors. First, phyllosilicates are generally characterized by only one cleavage plane, i.e., the perfect cleavage along the (001) basal surface. Whereas other faces often occur as preferred growth surfaces, in the case of macroscopic phyllosilicic crystals (e.g., micas) these are usually too narrow or rough for AFM analysis. Zones of mechanical weakness within micas run parallel to the preferred growth faces (Bloss et al. 1959; Klein and Hurlbut 1993), but the small-scale step features generated by cleaving these minerals are generally not euhedral, and hence the “edge” faces available for examination by AFM are randomly oriented surfaces. This makes possible the comparison of the reactivity of non-spe-