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 (trioctahedral) 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 $6\times$ 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 $(1\overline{1}0)$ 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 $(1\overline{1}0)$ 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 $(1\overline{1}0)$ 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.