In situ observations of muscovite dissolution under alkaline conditions at 25–50 °C by AFM with an air/fluid heater system

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ABSTRACT

Dissolution behavior of muscovite under alkaline conditions at 25–50 °C was investigated using in situ atomic force microscopy (AFM) with an air/fluid heater system to derive reliable dissolution rates and determine the dissolution mechanism and the effect of temperature on the dissolution rates. The muscovite dissolution took place only at the edge surfaces that are less than a few percent of the total surface area (TSA), while the basal surfaces were completely unreactive. During the initial stage of the experiments, some rough edge surfaces of muscovite dissolved much faster at the reactive site and appeared to straighten. The straightened edge surfaces seemed to retreat with a lower constant rate, which may correspond to the actual dissolution rate of muscovite, in the late stage. The edge surface area (ESA)-normalized dissolution rate at a certain pH and temperature condition, therefore, has a constant value independent of the size of etch pit or island (particle). The ESA-normalized dissolution rates derived from this AFM study were consistent with the dissolution rates renormalized to the estimated ESA of the earlier studies. In contrast, the TSA-normalized dissolution rates varied with the size of etch pit or island.

The activation energy for muscovite dissolution under alkaline conditions was very close to that for montmorillonite and illite dissolution. A model dissolution rate equation, which simultaneously includes the effect of pH and temperature, was deduced from the effect of pH on the activation energy, the rate equation of muscovite dissolution at 25 °C, and the Arrhenius equation. The dissolution rates estimated from the model were in good agreement with the experimental rates from 25 to 70 °C. The dissolution reaction order with respect to hydroxyl activity (or pH) increases with temperature.

Keywords: Muscovite, AFM, dissolution kinetics, dissolution mechanism, surface studies, hot-stage AFM

INTRODUCTION

Muscovite, a 2:1 dioctahedral phyllosilicate mineral, is one of the main rock-forming minerals, and is also common in sediments and soils. The dissolution or hydrolysis of muscovite provides K and Al in soil and often produces clay minerals such as smectite and kaolinite (Chamley 1989). Therefore, the study on the dissolution mechanisms and kinetics of muscovite is very important for the understanding of natural weathering and geochemical evolution of the Earth’s surface.

The dissolution mechanisms and kinetics of smectite and its related minerals, especially under alkaline conditions, have been the subject of many recent studies, because these minerals have been recognized as suitable materials for the engineering barrier designed for storage of high-level nuclear wastes in underground repositories (Bauer and Berger 1998; Cama et al. 2000; Huertas et al. 2001; Claret et al. 2002; Yokoyama et al. 2005; Kuwahara 2006a, 2006b). Recently, Köhler et al. (2003) and Kuwahara (2006a, 2006b) suggested that the dissolution rates of illite under alkaline conditions are similar to those of montmorillonite and that the dissolution mechanisms of both these minerals are most likely identical. However, the relation between muscovite and other 2:1 dioctahedral phyllosilicates, such as illite and montmorillonite, with respect to dissolution mechanisms and kinetics under alkaline conditions are not well understood, because data on the dissolution reaction of muscovite are scarce. In addition, the dissolution rates of muscovite reported in the previous studies are not consistent with each other (e.g., at pH ≈ 11, the dissolution rate at 25 °C reported by Nickel 1973 and that at 70 °C reported by Knauss and Wolery 1989 are almost the same). Such problematic dissolution rates of muscovite have been used for recent modeling studies of the interaction of host rocks or bentonite with hyperalkaline fluids (e.g., Savage et al. 2002; Hoch et al. 2004).

The dissolution rates of phyllosilicates have been derived from macroscopic wet chemical data from laboratory experiments (e.g., Bauer and Berger 1998; Cama et al. 2000; Huertas et al. 2001; Claret et al. 2002). These data, however, do not directly provide the dissolution mechanisms (Bosbach et al. 2000). In such studies, the N₂ BET surface area of the earlier studies. In contrast, the TSA-normalized dissolution rates varied with the size of etch pit or island.

The activation energy for muscovite dissolution under alkaline conditions was very close to that for montmorillonite and illite dissolution. A model dissolution rate equation, which simultaneously includes the effect of pH and temperature, was deduced from the effect of pH on the activation energy, the rate equation of muscovite dissolution at 25 °C, and the Arrhenius equation. The dissolution rates estimated from the model were in good agreement with the experimental rates from 25 to 70 °C. The dissolution reaction order with respect to hydroxyl activity (or pH) increases with temperature.

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