

# An Experimental Study of the Dissolution Mechanism and Rates of Muscovite

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This study represents a continuation of our efforts to characterize the dissolution rates and mechanisms of the major rock forming minerals. This work has shown that the dissolution mechanisms of multi-oxide minerals can be considered to consist of a sequential series of metal-proton exchange reactions, each releasing different metals into solution until the mineral structure is destroyed. Within the framework of transition state theory, the overall far from equilibrium dissolution rate is proportional to the concentration of the rate controlling precursor complex, which consists of the last viable structure in the exchange reaction sequence. The variation of precursor complex concentration, and thus dissolution rates, with solution composition can be deduced from the law of mass action for all of the exchange reactions involved in creating the precursor complex. Owing to the stoichiometry of the exchange reactions, the precursor complex concentration and dissolution rates decrease with the aqueous activities of all metals removed via the precursor forming exchange reactions.

Consideration of the dissolution mechanisms of a variety of major silicate minerals, the relative rate of metal-oxygen bond breaking in the muscovite structure is  $K >$  tetrahedral  $Al >$   $Si >$  octahedral  $Al$  (see Oelkers et al., 1999). As octahedral  $Al$  sheets represent a viable structure, they represent the precursor complex for muscovite dissolution. The concentration of this precursor complex, and thus the overall far from equilibrium muscovite dissolution rate is inversely proportional to the aqueous activities of  $K$ ,  $Al$ , and  $Si$ . Steady state muscovite dissolution rates have been measured at 150°C as a function of reactive solution  $pH$ , and  $K$ ,  $Si$ , and  $Al$  concentrations. The muscovite used in these experiments were obtained from a Madagascar pegmatite and has a composition consistent with  $(Na_{0.10}, K_{0.94})Fe_{0.17}Al_{2.88}Si_{3.30}O_{10}(OH_{1.80}, F_{0.19})$ . All experiments were performed in titanium mixed flow reactors. Steady state dissolution was stoichiometric; all reactive solutions were undersaturated with respect to secondary product phases and at far from equilibrium conditions with respect to muscovite.

Steady state rates measured at a constant aqueous  $K$  concentration of 0.01 mol/kg and nearly constant ionic strength are found to decrease with both aqueous  $Al$  and  $Si$  concentration. The  $pH$  variation of these rates is closely consistent with those previously reported by Knauss and Wolery (1989) at 70°C; they decrease sharply with increasing  $pH$  at acidic conditions but increase more gradually with increasing  $pH$  at basic conditions. The dependence of measured constant aqueous  $K$  concentration rates on  $pH$ , and reactive fluid  $Al$  and  $Si$  activity can be accurately described using

$$r_+ = k s (a_{H^+}^3/a_{Al^{+3}})^{(1/3)} a_{SiO_2}^{-1},$$

where  $r_+$  refers to the far from equilibrium muscovite dissolution rate,  $k$  designates a rate constant,  $s$  stands for the muscovite surface area, and  $a_i$  represents the activity of the subscripted aqueous species. The observed anticlinal variation of measured muscovite dissolution rates with  $pH$  stems from the affect on  $a_{Al^{+3}}$  of aqueous aluminum hydroxide complexes formation (e.g.  $AlOH_2^+$ ,  $Al(OH)_2^+$ , etc.) The 3:1 ratio of the relative effect of  $Si$  versus  $Al$  on muscovite dissolution rates may stem from the corresponding  $Si/Al$  atomic ratio of the tetrahedral sheet removed to form the partially detached  $Al$ -octahedral sheet corresponding to the precursor complex.

Among the consequences of the strong decrease of muscovite rates with increasing aqueous  $Al$  and  $Si$  concentrations are that 1) its dissolution rates will appear to depend on chemical affinity at far from equilibrium conditions, 2) its dissolution rates will never reach steady state in closed system reactors, and 3) any aqueous anion which tends to complex  $Si$  or  $Al$  in solution (such as organic acids at mildly acidic conditions) will increase muscovite dissolution rates. Because of the strong effect of aqueous  $Si$  on its dissolution rates, muscovite dissolution will be far slower in sedimentary basins than many other aluminosilicate minerals, such as the alkali-feldspars, whose rates are independent of aqueous  $Si$ . This observation may account for muscovite's persistence in sandstones with what appears to be incompatible mineral assemblages over timeframes in excess of tens of millions of years.

Nevertheless, any conclusions based on comparisons of literature kinetic rate data, such as those presented above, should be carefully tested by performing a set of consistent rate measurements of quartz as well as the other major rock forming minerals. Clearly, inconsistencies among rates reported in different studies may stem from differences in 1) solid preparation, 2) experimental techniques used to measure rates, 3) surface area measurements, 4) the amount of time waited prior to the investigator declares their experiments to be at steady state, and 5) improvements in analytical techniques. Until the origin of these and other possible inconsistencies among dissolution rates reported in the literature are resolved it will not be possible to precisely determine the extent and consequences of mineral dissolution rate variations over historic time.

Oelkers EH, Gislason SR, & Schott J, *Geochemistry of the Earth's Surface*; A.A. Balkema, 413-416, (1999).