

micas was determined by ICP spectroscopy. Specific surface areas and basal spacings of reacted micas were obtained by N₂-adsorption and x-ray powder diffraction, respectively.

Results

An initial period with rapidly decreasing rates common to most silicate dissolution experiments was observed during the first 300 h at pH 1 to 3 and up to 1400 h at pH 4. With increasing reaction time the release rates tend to reach a stable value, but atomic ratios of released elements remained in general non-stoichiometric with respect to the mineral composition up to 2800 h. Thus the dissolution process did not reach steady-state, e. g. significant differences in detachment rates of ions from different crystallographic sites were observed.

The release ratios of elements that were obtained during the stage of stable dissolution rates are shown in Table 1 together with the respective atomic ratios in the three micas. For biotite Al/Si ratios are higher than the bulk value except at pH 4. Higher than bulk Mg/Si, Fe²⁺/Si and K/Si ratios are obtained in all biotite experiments. The ratios of Mg/Fe^{tot} are, however, very close to the bulk value except at pH 4. The Fe²⁺/Fe³⁺ ratios have a tendency to increase with H⁺-activity and they also show that Fe²⁺ preferentially is leached from the mineral. In experiments with phlogopite the Al/Si release ratios were lower than the bulk mineral value at pH 4 and 3. The bulk value was exceeded at pH 2. Mg/Si release is close to stoichiometric ratios except at pH 2, where Mg release is significantly preferential with respect to Si. Selective leaching of K takes place except at pH 1. The K/Si non-stoichiometry is highest for phlogopite among the three micas. Muscovite releases an excess of Si with respect to Al. The selective leaching of interlayer K is significant only at pH 2 and 3.

Due to significant changes in mass and specific surface area during an experiment an 'initial' (and usually maximum) and a 'final' (and usually minimum) rate are presented. The 'initial' rate is based on the best estimate of sample weight during stable conditions and the initial specific surface area. The final rate is obtained using the same mineral weights but the final specific surface area.

The apparent reaction rates in acid solution can be approximated by an expression of the form:

$$R = k_{H^+} a_{H^+}^n$$

where k_{H^+} is an apparent rate constant for acid solutions, a_{H^+} represents the hydrogen ion activity and n an experimentally determined factor. Linear regression calculations for 'final' surface area normalized rates give values for k_{H^+} of

$8.1 \cdot 10^{-11}$, $6.6 \cdot 10^{-11}$ and $1.7 \cdot 10^{-12}$ for biotite, phlogopite and muscovite, respectively, in units of mol m⁻² sec⁻¹. The reaction order with respect to hydrogen ion, n , for the same minerals is 0.47, 0.49 and 0.20. Initial surface area normalized rates give values of $4.2 \cdot 10^{-10}$, $2.4 \cdot 10^{-11}$ and $1.6 \cdot 10^{-12}$ for k_{H^+} and 0.60, 0.36 and 0.15 for n for the different micas.

No expanded layers are found by XRD in dioctahedral muscovite after any experiment. Phlogopite showed additional peaks at $\sim 11.8 \text{ \AA}$ after reaction at pH 1 and 2. Biotite layers expanded at pH 3 (13.8 \AA) and 2 and reaction at pH 1 resulted in a large fraction of amorphous material.

Discussion

The order of susceptibility to weathering which is inferred from e. g. soil environments with reactivity of biotite \gg muscovite is in large confirmed by this study. It should be noted, however, that the rates of the three micas converge toward higher pH due to significant differences in pH-dependence. Considering surface area normalized rates of micas, great caution should be exercised when comparing rates with other silicates or rates obtained with different size fractions. This is due to that the present results support the hypothesis that mica dissolution proceeds mainly by detachment of atoms that are exposed at 'edge' $hk0$ surfaces. Thus the contribution of basal surfaces, either produced by grinding or by delamination during the experiment, to the total surface area adds very little to the total number of 'reactive' sites. Positive correlation of mica reactivity to grain size, as reported by numerous soil scientists, is likely to be explained by the anisotropic distribution of reactive sites on layer silicates.

The release ratios suggest that resistance to weathering increases in the order interlayer cation < octahedral cation < tetrahedral sheet for trioctahedral micas at pH ≤ 3 . The release of Mg and Fe^{tot} from the octahedral sheet of biotite at stoichiometric ratios with concomitant excess release of Fe²⁺ suggests a similar mechanism as proposed by White and Yee (1985) for coupling of redox reactions between surface adsorbed cations and Fe-containing silicates.

References

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