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Experimental study of the effect of pH on the montmorillonite dissolution kinetics at 25ºC

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Clay minerals play a major role in controlling chemistry of numerous natural systems. Interpretation and modeling of the geological and environmental processes strongly depend on our understanding of the environmental parameters that control the rates of dissolution/precipitation.

The overall goal of this work is to improve understanding of the dissolution rates of smectite at different pH conditions. Slightly acidic and alkaline conditions are common in nature and hyperalkaline solutions may occur in waste repositories due to the use of concrete as building materials. The effect of pH on the dissolution rate of montmorillonite was investigated using continuously-stirred flow-through reactors at 25ºC and buffered solutions (pH 4-13.5).

Steady-state dissolution rates for Si and Al exhibited a minimum of $\log r = -14.21$ mol/m^{2}s at pH ≈ 6.2, and they increase with both increasing and decreasing pH within the range studied. An additional inflection point is observed at pH 11-11.5, which allows us to identify three intervals of specific dependence of the smectite dissolution rate on the pH. The proton/hydroxyl promoted dissolution rates for these intervals are the following:

pH < 6.2	$\log r = -12.93 - 0.21$ pH
pH 6.2 - 11	$\log r = -14.86 + 0.099$ pH
pH > 11	$\log r = -17.54 + 0.33$ pH

Changes in the slope of the log rate-pH pattern may indicate that at least three different surface sites are involved in the reactions that control the montmorillonite dissolution mechanism.

The montmorillonite dissolution rates obtained in this study are similar to other rates obtained for smectite [1], illite [2] and kaolinite [3]. It suggests that, despite the differences in composition and structure, the rate limiting step and the dissolution mechanism may be similar.

References

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Experimental dissolution of basaltic glass; effect of pH, oxalic acid and temperature

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Experimental alteration of synthetic basaltic glass is performed. Three different batch-experiments are conducted to investigate the effect of pH (2-10), oxalic acid (10^{-3}M), and temperature (20-60^{o}C) on mechanisms and rate of alteration and element mobilisation. Textural and geochemical changes are documented by scanning and transmission electron microscopy (SEM and TEM) and x-ray spectroscopy (EDS and EPMA) at different times of reaction (2 h-13.5 months).

Incongruent dissolution is the dominant dissolution mechanism at pH ≤ 4 at 20^o, creating a residual rim in the glass surface, leached in Na, Mg, Ca, Al and Fe and passively enriched in Si and Ti. The Si(Ti) network is stable at pH 2, but becomes unstable and collapses with increasing pH and/or time, and Ti and Fe precipitates as secondary products.

Congruent dissolution is the dominant dissolution mechanism at pH 5-10 and at 20^o, and at 30^o and 40^{o}C at near neutral pH conditions. The process results in a decomposition of the glass network structure, and redeposition of secondary phases composed of Fe, Ti and Al.

Proton-promoted dissolution is more effective than ligand-promoted dissolution at pH ≤ 3. Ligand-promoted dissolution is, however, most efficient at pH 4-6/7, and entails increased selective dissolution up to pH ~5. Selective dissolution is also enhanced by increasing the temperature from 40^o to 50^{o}C.

Ligand-promoted dissolution results in development of elongated and hemispherical etch marks in the glass surface. The formation of such marks has previous been interpreted as microbial catalysed dissolution. This study indicates that the formation of such marks are a result of ligands in the solution, and do not necessarily require direct contact between glass and active cells.

At 20^{o}C the dissolution rate is pH-dependent, and increases with increasing and decreasing pH from a minimum at near-neutral pH (~5-6/7). Cracking and spallation off of the residual glass in the solution, results in an exposure of fresh glass surface at different reaction times. This gives a stepwise regulation of the dissolution rate. The dissolution rate increases exponential with increasing temperature, and a significant increase is observed from 40^o to 50^{o}C. This is probably caused by a change in the mechanism from congruent to incongruent dissolution.

Changes in solution-pH and temperature entail variable element mobilisation and mechanism of reactions, and may thus explain the variable composition of natural altered glass.