

Influence of NH_4^+ on the dissolution rate of smectites at pH 7

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Ammonium is a weak acid that in neutral environments, where the concentration of hydronium is very low ($<10^{-7}$ M), may contribute to the overall acidity of the solution. In such conditions ammonium may act as proton donor in mineral alteration processes. High concentrations of ammonium ions have been detected in a wide variety of diagenetic environments [1,2], but the effect of this ion on the smectite dissolution reaction at pH~7 is yet unknown. In order to quantify the possible influence of NH_4 , a series of flow-through dissolution experiments were carried out at 25, 50 and 70 °C, and five NH_4 concentrations (10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} and 0.5 M) until a steady-state dissolution rate was reached.

The results show that at 25 and 50 °C the smectites dissolution rate, derived from Si concentration in the output solutions, increases with ammonium concentration. However, at 70 °C the dissolution rate is approximately constant, irrespective of ammonium concentration.

The evolution of the Al/Si ratio shows a linear dependence on the ammonium concentration, independent of temperature. As the ammonium concentration decreases, the Al/Si ratio tends to stoichiometry, i.e. the amount of Al increases in the output solutions. This trend may be explained by precipitation of aluminum hydroxides. Figueras et al [3] observed that NH_4 favored the formation of Al-hydroxide pillars in the interlayer space of smectites at circumneutral conditions. Currently, we are conducting detailed studies on the altered smectites to fully understand the reaction mechanisms.

[1] Bates et al., *Chem. Geol.* **284**, 2011. [2] Collins., *Geochemistry of Oilfield Waters*, 1975. [3] Figueras et al., *Clays Clay Miner* **38**, 1990.