An experimental study of sepiolite dissolution rates and mechanisms at 25 °C

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Two distinct models have been proposed to explain non-stoichiometric dissolution of multi-oxide silicate minerals: it is either attributed to leaching of divalent metals from the mineral structure or to an interface coupled dissolution-precipitation mechanism. This study aims to provide insight in the dissolution mechanisms of multi-oxide silicates by assessing the dissolution rates and behaviour of sepiolite, a Mg-rich 2:1 trioctahedral clay. This clay is characterized by continuous inverted tetrahedral sheets and discontinuous octahedral sheets, forming channels. Steady state dissolution rates (r_+ in mol/cm^2/s) of sepiolite were determined as a function of pH from mixed flow reactor experiments based on the Si release rate at 25 °C and are described by $r_+ = 10^{-16.08}(15(a_{2H^+}/a_{Mg^{2+}})^{1/6}/(1+15(a_{2H^+}/aMg^{2+})^{1/6}))$. This rate equation is consistent with a dissolution mechanism of sepiolite by which interstitial Mg is exchanged for H^+, followed by the relatively slow release of Si. Dissolution at pH ≤5.5 and pH ≥9.25 was found to be non-stoichiometric: Mg is preferentially released at low pH and relatively more Si is released at high pH. To examine the extent of non-stoichiometric dissolution and its implications on solid phase transformations, batch experiments were performed. From mass balance calculations, Energy-Dispersive X-ray spectroscopy (EDS) and X-Ray powder Diffraction (XRD), it can be inferred that after 688 hours at pH 2.57, 98% of the Mg was removed from the solid sepiolite structure, while 80% of the SiO_2 was retained in a solid phase. The batch experiments demonstrate that non-stoichiometric steady state dissolution leads to the formation of an extensive Mg depleted layer. In concurrence with the Si-release rates at low pH, the Mg-free layer is interpreted to have a similar structure to amorphous SiO_2. Partial preservation of the structural integrity of the SiO_2 layer implicates non-stoichiometric dissolution via leaching, rather than dissolution – reprecipititation. Continuous non-stoichiometric metal release from sepiolite is likely facilitated by its channel-like structure which allows for the transport of Mg, without breaking the Si-tetrahedra.