Linking nm-scale characterizations of altered silicate surface to macroscopic dissolution rate laws: New insights based on diopside

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The interfacial zone between a bulk fluid and a mineral surface is where all exchange of matter and energy occurs during chemical weathering. However, our knowledge is still limited with respect to understanding where and how the rate-determining dissolution reactions take place. A complicating factor is the commonplace formation of amorphous Si-rich surface layers (ASSL), which may hinder contact between the fluid and the mineral surface. Previous studies showed that the protective ability of ASSL critically depended on properties inherited from the parent silicate mineral, which remain yet to be unraveled.

To address the role of ASSL, we investigated the dissolution of a common silicate (diopside), and related the bulk dissolution rate (determined in classical flow-through experiments) with the nanoscale dissolution rate and surface chemistry of its individual prevalent faces (by combining vertical scanning interferometry (VSI) measurements of the topography of reacted cleavages and transmission electron microscopy (TEM) characterizations of the ASSL). While ASSL were evidenced on all of the investigated faces, only those formed on (110) and (1-10) were passivating, thereby controlling the reactivity of the underlying faces. The (110) and (1-10) faces intersect the highest density of Mg-O-Si and Fe-O-Si bonds, and this specificity may explain the passivating behavior of the corresponding ASSL. Moreover, we evidenced an inverse relation between aqueous silica concentration and the bulk dissolution rate of crushed diopside grains, which suggest that the (110) and (1-10) faces are predominant in a powder. By considering ASSL as a separate phase that can control silicate dissolution rates, extrapolated laboratory-based rates at conditions relevant to the field can be lowered by up to several orders of magnitude, thereby decreasing the large gap between laboratory and natural rates. This has important implications for more accurately modeling chemical weathering reactions.

In situ real time infrared spectroscopy study of (poly)molybdate ions sorption into layered double hydroxides

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Due to the high anion-exchange capacities (2-3 meq/g) and their relatively low cost, layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds (described with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}.mH_2O$) have been studied for application in wastewater treatment by intercalated oxyanions [1,2].

The aim of this study was to investigate the sorption mechanism of molybdate anion and to obtain the speciation of molybdate inside the LDH structure after sorption in a Zn/Al sulphate-carbonate LDH.

To the best of our knowledge, it is the first time that sorption of molybdate anion into layered double hydroxides is studied by attenuated total reflection (ATR) FTIR spectroscopy [3]. *in situ* analysis of the sorption processes into the LDHs interlayer (exchanged of (poly)molybdate ions with sulfate or carbonate ions) allowed us to identify the high affinity of LDH towards $Mo_7O_{24}^{6-}$, which sorbs even though it is a minor species in comparison with other protonated heptamolybdate ions.

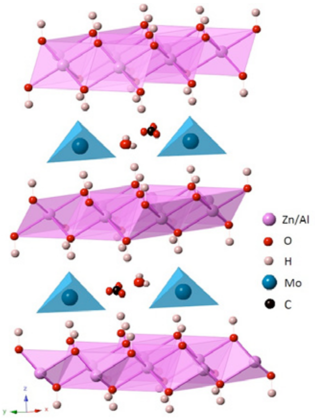

Figure 1: Structure of a layered double hydroxide, with interlayer molybdate and carbonate anions.

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