Kinetics and mechanisms of Ni sorption by nanocrystalline vernadite

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Vernadite is a nanocrystalline Mn oxide that is ubiquitous in the environment, being found for example in soils and sediments. Its structure consists in the turbostratic stacking of layers separated from each other by hydrated interlayer cations. Theses layers, built of edge-sharing $(Mn^{4+}O_6)^{8-}$ octahedra, contain vacancies and isomorphic substitutions that provide vernadite with a high layer charge deficit. As a consequence of this charge of its nanocrystallinity, vernadite is observed to control or influence the fate of many trace metals in the environment. Despite these observed associations, the kinetics and mechanisms of interactions between vernadite and metals are still poorly contrained. We studied [1], at pH 5.8 and $I = 0.1$ M NaCl, the *in situ* kinetics and mechanisms of Ni^{2+} uptake by synthetic vernadite using wet chemistry, atomic-resolution scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS) and synchrotron high-energy X-ray scattering (HEXS) in both the Bragg-rod and pair distribution function formalisms. According to HEXS and STEM-EELS, Ni^{2+} adopted mainly a triple-corner sharing configuration above layer vacancies, and had a Debye-Waller factor about four times higher than layer Mn. Steady-state was reached after ~2.2 h of contact time. Atomic-scale imaging of the solids also evinced the presence of minor Ni adsorbed at the crystal edge. The retention coefficient was $R_D=10^{3.76\pm0.06}$ L kg^{-1}, in agreement with literature data.

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References

[1] Grangeon *et al.* (2017) *Chemical Geology*, in press (doi:10.1016/j.chemgeo.2017.03.035).