A computational study of the initial stage of nucleation of heavy metal cations on clay edges

CHI ZHANG[1], XIANDONG LIU*[1], XIANCAI LU[1]

[1] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210046, P. R. China
(*corresponding: xiandongliu@gmail.com)

Adsorption of heavy metal cations on clay surfaces is greatly pH-dependent. At high pH and metal concentration, surface complexation on clay edge surfaces can yield nucleation and precipitation of new phases including hydroxides and phyllosilicates. These nucleation processes are typically surface-induced. Such heterogeneous nucleation is more common than the homogeneous in nature. In order to reveal the microscopic mechanism of the early stage in the nucleation of heavy metals on clay edges, we performed first principles molecular dynamics (FPMD) simulations systematically to characterize the chemistry of the incipient clustering processes.

First, we looked at the nucleation of hydroxide, i.e. without silicon. We took Pb2+ and Ni2+ as the model cations because they have different behaviors: as experiments have shown the former does not nucleat on clay edges but the latter does. With detailed analyses, we found that Pb2+ and Ni2+ have different complexation mechanisms: Pb2+ cations are adsorbed onto different sites with the similar probability whereas Ni2+ cations prefer octahedral vacancy to the other sites. pKa calculations indicate that Ni2+ adions can provide OH- groups for complexing the subsequent cations through hydrolysis, which can thus result in nucleation and precipitation eventually. In contrast, the first adsorbed Pb2+ cannot provide available complexing sites due to the extremely high pKa, thus making nucleation impossible. On the basis of the study of Ni2+, we moved on to the case with the presence of silicic acid, which led to the formation of phyllosilicates. We evaluated the free energies of complexation of silicate anions. By comparing various complexation processes, the favored pathway and the effect of clay surfaces has been revealed.

Our findings reveal the role of the surface in heterogeneous nucleation, which should apply to other similar systems. The results are directly useful for understanding the fate of heavy metals on the Earth’s surface.