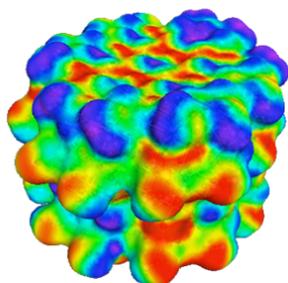


Predicting the protonation behavior of the kaolinite surface

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Clay minerals, known for their ion exchange capacity, have an impact on environmental issues such as uptake of contaminants from ground water and retention of oil in reservoirs. Kaolinite is believed to play an important role in enhancing oil recovery by low salinity water flooding, where decreasing Ca^{2+} and Mg^{2+} concentrations in the injected solution increases the amount of oil that can be generated from sandstone reservoirs. The ability of kaolinite to act as an ion exchanger depends on its atomic surface structure, pH and in particular, on its protonation state. This is especially true for metal ions, which compete with protons for bonding sites on surface oxygens.



COSMO surface of the kaolinite cluster model

We have used the implicit solvent model, COSMO-RS, to predict the pK_a values of kaolinite surfaces, using a molecular cluster consisting of 512 atoms, to represent a kaolinite surface. Using a cluster allows us to determine basal plane and edge protonation properties using the same model. We found that the pK_a values could be classified

according to surface composition. Al-OH_2 groups had a median pK_a value of 5.5 and were generally more acidic than SiOH groups with a median pK_a value of 10.6. The standard deviation was 2 to 3 pH units for most surface sites. Using our calculated pK_a values, we were able to estimate the point of zero charge (PZC) for kaolinite for the various surface sites, which has been difficult or impossible, using experimental approaches. The kaolinite edge has a PZC of 3.7 and the AlOH basal plane a PZC of 7.7. This has the consequence that the PZC for kaolinite samples ranges between 4 and 6 and is geometry dependent... Higher values are found for flat particles where the basal plane behavior dominates over edge effects. Our results help explain why the PZC of kaolinite can differ significantly depending on the nature of the kaolinite samples (i.e. the surface to edge ratio, the diameter of particles) used in experiments.

Phase transition in aluminous silica at lowermost mantle P-T conditions

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Using Al-bearing SiO_2 glasses with 4 and 6 wt% Al_2O_3 as starting materials, we investigated the phase transition from the CaCl_2 -structured to the $\alpha\text{-PbO}_2$ -structured phase (seifertite) at pressures and temperatures corresponding to the lowermost mantle. The experiments were conducted with synchrotron-based *in situ* X-ray diffraction in the laser-heated diamond anvil cell. The transition from the CaCl_2 -structured phase to seifertite occurs between 113 and 119 GPa at 2500 K. Comparison with previous results shows a decrease of the transition pressure with increasing Al-content. A tentative phase diagram reports the minerals compositions as a function of pressure in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system. This diagram includes a binary loop compatible with an Al partition coefficient between CaCl_2 -form and seifertite between 0.55(5) and 1.

Based on the X-ray pattern refinement, our samples show a very small 0.3(2) % volume decrease across the transition. Still, the transition could very well be associated with a more significant change in density if the Al substitution mechanisms are different in CaCl_2 -form and seifertite. The most likely situation is that Al-substitution occurs via O-vacancies in the CaCl_2 -form and via extra interstitial Al in seifertite. That would result in a $\sim 1.5\text{-}2.0$ % density increase at the transition pressure for silica containing 5 wt% Al_2O_3 . This value is of the same order of magnitude than the estimated difference in density between peridotitic mantle and basaltic lithologies in the lowermost mantle.