

The pyrophyllitic substitution: Atomistic investigation, implications on the stability of micas and clays, and why interlayer water matters

BENOIT DUBACQ^{1*}, OLIVIER VIDAL² AND ERIC LEWIN²

¹Univ. of Cambridge, Dept. Earth Sciences, Downing Street,
Cambridge, CB2 3EQ, United Kingdom
(*correspondence: bd298@cam.ac.uk)

²LGCA UMR 5025, 1381 rue de la Piscine, 38400 Saint-
Martin d'Herès

Predicting phase relations and reactions involving clay minerals is of critical importance when modelling geological reservoirs and making thermobarometric estimates at temperatures inferior to 350°C. Applying simple oxide summation techniques is insufficient to estimate the thermodynamic properties of these phases with a satisfactory precision; more sophisticated numerical techniques are required when experimental results are not available. Recent atomistic techniques allow constraining activity models independently from kinetics. Amongst the various solid solutions occurring in phyllosilicates, the magnitude and the thermodynamic significance of the pyrophyllitic substitution have strong implications on the stability of clay minerals at surface conditions. We have applied a lattice energy estimation method combined with Monte Carlo simulations to estimate the energy of mixing along the muscovite-pyrophyllite solid solution. The results show a positive and asymmetric Gibbs free energy of mixing, concordant at first order with previous thermodynamic models issued from phase relations in micas and with field observations. This implies that minerals with compositions intermediate to pyrophyllite and muscovite are unstable at low temperatures, suggesting that illites and smectites are metastable phases. However, clay minerals also contain water in interlayer position, and phase relations and experimental results suggest that its incorporation competes with the non-ideal pyrophyllitic substitution to stabilize these phases at surface conditions.

The structure and reactivity of cobalt-siderophore complexes

OWEN W. DUCKWORTH^{1*}, YUQIANG BI²,
ANDRZEJ A. JARZECKI³ AND JOHN R. BARGAR⁴

¹North Carolina State University, Raleigh, NC 27695-7619
(*correspondence: owen_duckworth@ncsu.edu)

²The University of Michigan, Ann Arbor, MI 48109-2125

³The Brooklyn College and the Graduate School of the City
University of New York, Brooklyn, NY 11210

⁴Stanford Synchrotron Radiation Lightsource, Menlo Park,
California 94025

Biomolecules have a significant impact on the fate and transport of contaminant metals in soils and natural waters. Siderophores, biogenic chelating agents with high affinities for iron that are exuded by microbes and plants, may also form strong complexes with contaminant metals [1]. Specifically, we have recently demonstrated that siderophores may form complexes with Co (III) that possess higher stability constants than the corresponding Fe (III) complexes [2]. This observation suggests that siderophores may play a role similar to synthetic chelating agents in the dispersion of cobalt in contaminated sites.

To better understand the possible effects of siderophores on cobalt mobility, we conducted a series of spectroscopic, computational, and chemical experiments to characterize the stability and structure of Co-siderophore complexes and to elucidate the mechanisms of their formation and degradation in the environment. Experiments conducted using the model siderophore desferrioxamine B (DFOB) have shown that siderophores may solubilize cobalt from mineral phases, resulting in dissolved Co (III)HDFOB⁺ complexes and Co (II). Dissolution rates from heterogenite (CoOOH) are significantly greater than those of goethite (FeOOH) at corresponding conditions, suggesting a strong kinetic preference for cobalt solubilization. The resulting Co (III)HDFOB⁺ complexes may also sorb to the surfaces of metal oxides in a manner similar to that of Fe (III)HDFOB⁺ complexes [3], suggesting that minerals may be an important sink for Co-siderophore complexes. The results suggest that siderophores may play significant roles in regulating cobalt bioavailability, fate, and transport in the environment.

[1] Hernlem *et al.* (1999) *Water Resour.* **33**, 951–960.

[2] Duckworth *et al.* (2009) *Marine Chem.* **113**, 114–122.

[3] Duckworth *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 3371–3380.