Foreword to the Research Front on ‘Mineral–Organic Interactions in Aqueous Systems’

Jon Chorover

The mineral–water interface exhibits great diversity in surface functional group composition and associated reactivity towards inorganic and organic solutes that occur in natural soil, sediment and water.\(^1\) Chemical processes of environmental significance involving oxidation–reduction, adsorption–desorption, and dissolution–nucleation are promoted by these interfaces because of their propensity for acid–base, ion- or ligand-exchange, and redox reactions. Mineral surface hydroxyl groups of iron, aluminium and manganese (oxyhydr)oxides and siloxane groups of layered aluminosilicates, for example, are known to exhibit a range in affinities for reaction with protons, hydroxyl ions, metals, oxyanions, and aqueous organic species and their complexes.\(^3\)

The environmental implications of mineral surface chemistry are manifold and diverse. They include atmospheric CO\(_2\) drawdown associated with silicate mineral dissolution,\(^4,5\) removal from solution of adsorptive metal and oxyanion contaminants,\(^6\) nutrient retention for plant growth\(^7\) and organic matter stabilisation against microbial biodegradation.\(^8\) Through a combination of macroscopic experiments, molecular spectroscopy studies, and molecular modelling, environmental chemists are developing an improved understanding of the molecular-scale controls over the rates and extents of mineral surface reactions.

This Research Front presents six contributions discussing various aspects of mineral surface reactions and their environmental relevance using experimental, spectroscopic and simulation methods. The Research Front begins with a review by Casey\(^9\) on the mechanisms and kinetics of ligand exchange reactions at mineral surfaces. This paper discusses reactivity trends for ligand and oxygen isotope exchanges in nanometer-sized molecular clusters and larger mineral structures from the perspective of coordination chemistry. It provides examples of how an understanding of exchange reactions in the molecular clusters can shed light on reaction kinetics of broad environmental relevance, such as those for mineral dissolution and metal–ligand complex formation in aqueous solutions.

The second paper, a review by Stack and Kent,\(^10\) discusses how computational modelling, specifically molecular dynamics and quantum chemical simulations, can be used to build insightful kinetic models of mineral surface reactions. Illustrative examples are presented for water ligand exchange, adsorption, crystal growth, dissolution and electron transfer. Interfacial reactions are strongly affected by the speciation of aqueous phase reactants as shown in the third paper, authored by Carbonaro and Stone.\(^11\) This study, which evaluates mineral-surface-mediated rates of Cr\(^{III}\) oxidation to Cr\(^{VI}\) during surface reaction with hydrous Mn\(^{IV}\) oxide, shows that Cr\(^{III}\)-chelating ligands alter the pH-dependent kinetics of oxidation. This is important, because most soil systems contain natural organic matter (NOM) that can form stable complexes with polyvalent metals.

The fourth paper by Pasakarnis et al.\(^12\) builds on prior work of the Scherer group\(^13\) demonstrating electron transfer between adsorbed Fe\(^{III}\) and underlying Fe\(^{III}\) oxide surfaces. In the former paper, the authors obtained a combination of isotopic and spectroscopic data that show that introduction of NOM components can alter the Fe atom exchange rate – an observation that the authors argue has potential relevance to long-term, mineral-associated stabilisation of organic matter in soils. The issue of NOM stabilisation at mineral surfaces is explored further in the paper by Chen and Sparks.\(^14\) Employing STXM-NEXAFS spectroscopy to assess organo-mineral associations in soils from reducing environments depleted of Fe oxides, they found that NOM composition was highly variable at the submicrometre scale and exhibited no discernible pattern with inorganic element distributions. The sixth and final paper of the Research Front focuses on the role of mineral surface chemistry in adsorption of novel energetic compounds, a diverse class of emerging organic contaminants. The findings of Linker et al.\(^15\) highlight the importance of compatibility between the functional group chemistries of adsorbate and adsorbent in controlling the extent and hysteresis of the adsorption reaction.

Although this Research Front only ‘scratches the surface’ of work pertaining to the mineral–organic interface, I hope that it represents the multitude of interactions that are being probed using complementary experimental and modelling approaches. I thank all of the authors for their valuable contributions to this important area of research.

Jon Chorover
Editor, Environmental Chemistry

References


