

A kink-site limited model for growth and inhibition of biominerals

J.J. DE YOREO¹, A.A. CHERNOV², L.A. ZEPEDA-RUIZ¹,
L.E. WASYLENKI³, S. ELHADJ³, C.A. ORME, G. GILMER¹
AND P.M. DOVE³

¹Lawrence Livermore National Laboratory, Livermore, CA
(deyoreo1@llnl.gov, zepedaruiz1@llnl.gov,
orme1@llnl.gov, gilmer1@llnl.gov)

²NASA Marshall Space Flight Center, Huntsville, AL
(alex.chernov@msfc.nasa.gov)

³Virginia Polytechnic Institute, Blacksburg, VA
(dove@vt.edu, elhadj@vt.edu, waz@asu.edu)

One forefront of biomineralization science is the need for a fundamental understanding of kinetic and thermodynamic controls on the morphology and compositional signatures of minerals formed in complex systems. Conventional analysis of mineral growth from aqueous solutions has been based on application of the Gibbs-Thomson (GT) effect, a thermodynamic principle relating the size of atomic features on a crystal face to the driving force for crystallization. Experimental results obtained in recent years using atomic force microscopy (AFM) call into question the basic GT requirement that the thermal fluctuations along step edges on a crystal face are fast enough to assure that step growth is controlled by molecular incorporation at kink sites along the steps. Rather, the generation of the kinks themselves by so-called "1D nucleation" appears to become the rate limiting step.

Abandoning the GT effect helps to explain numerous anomalies observed during growth of sparingly soluble biominerals. Here we present the results of AFM studies of calcite and brushite growth that are best explained by assuming step motion is limited by kink availability. We show how they impact analyses of growth rates, extraction of thermodynamic parameters, and interpretation of impurity effects. We then show that, during the growth of calcite in the presence of inorganic and organic constituents important in the biogenic carbonates such as Sr²⁺ and a wide variety of aspartic acid-rich peptides, the dependence of step kinetics on impurity content and saturation state differs dramatically from that expected from the GT effect.

To explain these results we replace the GT-based analysis with a kinetic description in which the essential step in stopping growth is the blocking of newly formed kinks. Finally, we show the results of kinetic Monte Carlo simulations that predict behaviour similar to that seen in the AFM experiments, and explicitly reveal the importance of 1D nucleation and kink-site blocking during growth and inhibition.

Free energy of adsorption of molecules and ions at the calcite-water interface

SEBASTIEN KERISIT^{1,2} AND STEPHEN C. PARKER²

¹Pacific Northwest National Laboratory, 902 Battelle Blvd,
P.O. Box 999, K8-96, Richland, WA 99352, USA
(sebastien.kerisit@pnl.gov)

²Chemistry Department, University of Bath, Claverton Down,
Bath, BA2 7AY, UK (s.c.parker@bath.ac.uk)

A full atomistic understanding of adsorption and growth thermodynamics and kinetics requires the evaluation of the free energies of adsorption in aqueous solution. Currently, studies of adsorption and growth of inorganic solids have focused on computing the energetics of these processes.

In this presentation, we will show that these free energies can be calculated and we illustrate this by modeling the free energy profile of water on the surfaces of calcite. The approach uses molecular dynamics with parameterized equations to describe the interatomic forces. These simulations predict that the free energy of adsorption of water is relatively small (~3 kJ mol⁻¹) compared to the enthalpy of adsorption (~45 kJ mol⁻¹) calculated in a previous paper (Kerisit and Parker 2003). Hence, this suggests that a large change in entropy is associated with the water adsorption on the surface. To investigate this further, we computed the effect of the mineral surface on the water orientation and diffusion.

Next, we will present results obtained from the simulation of the adsorption of three metal ions (magnesium, calcium, and strontium) on the (10.4) calcite surface in aqueous solution. First, we will demonstrate that the potential model is able to reproduce the interactions between water and the metal ions regardless of whether they are at the mineral surface or in bulk water. Next, we will show that the free energy profile of an ion adsorbing on the surface correlates with the solvent density and that the formation of an inner-sphere complex is associated with a large free energy barrier, which is mainly electrostatic in nature. In addition, these calculations allow us to begin to address the rates of adsorption and desorption, which are essential for studying growth and dissolution. Our calculations of the rate of desorption from the surface suggest that magnesium has a much longer residence time on the surface than calcium and strontium due to its strong interactions with both water and the surface.

References

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Travertine formation and other pattern forming processes on sloping surfaces

BJØRN JAMTVEIT, ØYVIND HAMMER, MARK BUCHANAN, SIMON DEVILLIER, DAG DYSTHE, AND JENS FEDER

Physics of Geological Processes, University of Oslo, P.O. Box 1048 Blindern, N-0316 Oslo, Norway
(bjorn.jamtveit@geo.uio.no)

Carbonate precipitation around hot springs commonly produce spectacular terrace patterns on scales ranging from millimeters to meters (Fig.1). Similar patterns can be observed in a variety of other natural and synthetic systems where growth processes on sloping surfaces takes place in connection with fluid flow. The large-scale terraces (meter-scale) of major travertine deposits may result from positive feedbacks between local fluid flow velocities and the rate of carbonate precipitation. This feedback has been suggested to arise due to fluid flow controls on the rate of CO₂-loss. It would thus be specific to the carbonate system.

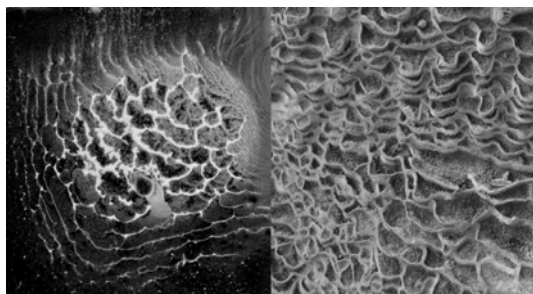


Figure 1. Left: Terrace-pattern formed during flow of water with suspended particles on a glass slide. Field of view ca. 2 cm. Right: Natural travertine terraces from the Arctic hot springs at Bockfjord, Svalbard. Field of view ca. 10 cm.

Smaller-scale terrace patterns with approximately constant step-heights may however be controlled by coupled flow and aggregation processes rather than carbonate precipitation. The structures forming are thus not specific for the water-carbonate system, but arise in a variety of systems with slow flow of particle laden fluids. We will present experimental and theoretical results that constrain the conditions under which such patterns form and what factors that affect their geometry.

Field and laboratory evidence of formation of uranyl phosphates within leached layers of dissolving apatite in undersaturated solutions

T. MURAKAMI¹ AND T. OHNUKI²

¹Department of Earth and Planetary Science, Univ. of Tokyo, Tokyo 113-0033, Japan (murakami@eps.s.u-tokyo.ac.jp)

²Advanced Science Research Center, JAERI, Ibaraki 319-1195, Japan (ohnuki@sparclt.tokai.jaeri.go.jp)

The formation of uranyl phosphates on the surface of dissolving apatite, Ca phosphate, in solutions undersaturated with respect to the uranyl phosphates was investigated in the field and laboratory to better understand mineral growth at mineral-water interfaces. Saleeite, Mg uranyl phosphate, was formed on the surface of apatite in the secondary U ore deposit at Koongarra, Australia. Saleeite replaced apatite completely in some cases. Thermodynamic calculations by EQ3NR revealed the bulk ground waters were undersaturated with respect to saleeite, which suggests local saturation for the formation mechanism. In the laboratory, 10 x 10 x 1-mm apatite samples reacted with 20 mL of uranyl solution of 4.0 x 10⁻⁴ mol/L U at pHs ranging from 2 to 4 and 25 °C for 10 days. A layer of autunite, Ca uranyl phosphate, was formed on the surface of apatite. The formation of autunite instead of saleeite occurred because of no availability of Mg. All solutions were undersaturated with respect to autunite. Rutherford backscattering spectrometry (RBS) revealed that the thickness of the autunite layer increased with increasing dissolution of apatite. RBS indicated that the autunite layer becomes thicker without increasing the distribution density of autunite in the autunite layer as the reaction proceeds. RBS also revealed that a leached layer of apatite, about 100 nm thick, was present between fresh apatite and the autunite layer, and characterized by a lower U concentration than that in the autunite layer and by higher and lower Ca concentrations than those in the autunite layer and apatite, respectively. Our results by RBS strongly suggest that the surface mineralization proceeds in the leached layer by local saturation and that autunite formed is finally added to and accumulated in the autunite layer, which also explains the saleeite formation in the fields. The present study demonstrated mineral growth at mineral-water interfaces in undersaturated solutions and long-term U fixation in a natural system.

Probing the reactivity of the dolomite-water interface using high resolution X-ray reflectivity

PAUL FENTER¹, Z. ZHANG¹, C. PARK¹, N.C. STURCHIO^{1,2},
X. HU AND S.R. HIGGINS³

¹Argonne National Laboratory, ER-203, Argonne, IL USA
(fenter@anl.gov, zhang@anl.gov, cpark@anl.gov)

²University of Illinois at Chicago, Chicago IL, USA
(sturchio@uic.edu)

³Wright State University, Dayton, OH USA
(xiaoming.hu@wright.edu, steven.higgins@wright.edu)

The interaction of cations with mineral-water interfaces is fundamental to our understanding of geochemical transport. A particularly rich range of phenomena has been observed in the interaction of metal cations with carbonate surfaces, including adsorption/incorporation of isolated ions, and growth of islands, and mono- and multi-layer films.

The interaction of dolomite surfaces with dolomite-supersaturated solutions is an area that is particularly difficult to understand. Previous AFM measurements have shown that dolomite surfaces in contact with supersaturated solutions grow thin (~1 or 2 layer) films that are largely inert with respect to further growth and whose thickness depend upon whether the solutions are rich in Ca or Mg [1]. Lateral force images suggest that the compositions of these layers depends upon the solution compositions, but the layer compositions cannot be determined by traditional measurements due to spectral interference from the substrate.

We have applied high resolution surface X-ray reflectivity to provide new insights about the structure and composition of the dolomite-water interface. Measurements in dolomite saturated solution (saturation index, SI=0) show that the dolomite surface is ideally terminated and has characteristics similar to those found previously for the calcite-water interface [2], including a slightly relaxed surface and a distinct surface hydration layer. Additional measurements in supersaturated solutions (SI = 2.3) rich in either Ca or Mg reveal the formation of continuous surface films whose thickness and electron density are controlled by the solution compositions. These data provide new, direct insight into the composition and reactivity of dolomite-water interfaces.

References

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Investigating the effect of calcium on barite (001) and (210) surfaces using *in situ* atomic force microscopy

K.J. FINCH¹, A.I.R. STARK¹, P.L. WINCOTT¹,
M.C. WARREN¹, I.R. COLLINS² AND D.J. VAUGHAN¹

¹Department of Earth Sciences and Williamson Research
Centre for Molecular Environmental Science, University
of Manchester, UK.

(katie.j.finch@student.manchester.ac.uk)

²Well Performance Team, BP International Limited, Chertsey
Road, Sunbury on Thames, Middlesex, UK.

Barite (BaSO₄) is a major component of the inorganic scale that forms in well bores and oilfield pipework due to its very low solubility. Currently, scaling is controlled by chemical inhibitors that work by inhibition of nucleation and growth retardation. However, for reasons that are poorly understood, these processes are affected by the presence of cations such as Ca²⁺, resulting in changes in barite crystal morphology. We seek to understand why these changes occur, and thus the mechanism and efficiency of growth inhibition.

Observations of barite crystals made in air using atomic force microscopy (AFM), show surfaces to be characterized by steps commensurate with the corresponding plane spacing ($d_{001} = 7 \text{ \AA}$ and $d_{210} = 3.5 \text{ \AA}$). Many of these steps are straight and parallel, while others meet at acute angles specific to that surface, suggesting some crystallographic control.

In situ AFM experiments have been used to study surface growth and dissolution processes in the presence of supersaturated solutions of BaSO₄. Recorded images show differences in growth on the (001) and (210) surfaces: growth island development and lateral nanoscale step edge advancement is seen on the (001) surface, and restricted linear step edge advancement on the (210) surface. In the presence of Ca²⁺, growth islands have a less uniform shape, and step edge advancement is less ordered. Some dissolution is observed on the (210) surface. In all experiments, increased rates of growth are observed with increasing ionic strength of solution.

Comparisons of experimental investigations with computer simulation models of barite surfaces, are being used to identify mechanisms of Ca²⁺ incorporation within the barite crystal structure, and to aid prediction of resulting crystal morphologies.

Non-stoichiometric mineral surfaces: *Ab initio* phase diagrams

STEPHEN C. PARKER¹, DAVID J. COOKE¹,
ARNAUD MARMIER¹ AND SEBASTIEN KERISIT^{1,2}

¹Department of Chemistry, University of Bath, BA2 7AY, UK
(s.c.parker@bath.ac.uk)

²Pacific Northwest National Laboratory, 902 Battelle Blvd,
P.O. box 999, K8-96, Richland, WA 99352, USA
(sebastien.kerisit@pnl.gov)

We present recent work applying *ab initio* electronic structure methods based on DFT to model non-stoichiometric surfaces of minerals in equilibrium with a vapour consisting of different gases. The stability of surfaces of different stoichiometry are compared in terms of general surface phase diagrams, initially as a function of the oxygen and hydrogen chemical potentials, which are themselves dependent on temperature and partial pressures of oxygen and hydrogen. Thus, the stable structures and compositions can be evaluated at specific experimental conditions. The major difficulty of applying this approach is the large amount of computer time required to simulate the different surface configurations. We will show how atomistic methods can be used to aid in the search of different surface configurations and to model the surface lattice dynamics, thus giving a good representation of the free energies involved.

We will describe three recent applications. First, we will report the surface compositions of the low index surfaces of Alumina in contact with oxygen, hydrogen or water. In each the results are in good agreement with experimental data. Secondly, we will discuss the predictions of the surface behaviour of the (10.0) and (11.0) surfaces of ZnO again in equilibrium with both the bulk structure and partial oxygen and hydrogen pressures. At ambient temperatures, we predict that molecular water will be present on the surface of the (10.0) whereas a hydroxide layer is favoured for the (11.0). A prediction also duplicated using atomistic, potential based, methods. The final application is where we begin to include other gases such as carbon dioxide in contact with mineral surfaces. The results on the (10.4) and (00.1) surfaces of calcite in the presence of water and carbon dioxide not only show that the surface stoichiometries are highly dependent on the partial gas pressures, and predicts new surface structures not previously considered.

Observing the chemical composition and the point of zero charge of mineral surfaces *in situ* under water by nonlinear optics

M. FLÖRSHEIMER, K. KRUSE, R. KLENZE
AND TH. FANGHÄNEL

Forschungszentrum Karlsruhe, Institut für Nukleare
Entsorgung, Karlsruhe, Germany (florshg@ine.fzk.de)

The properties of mineral/electrolyte interfaces are controlled by the surface functional species. In order to model surface reactivity and adsorption/desorption processes a large number of functional groups has been postulated. In most cases, however, a direct proof for the existence of these species in real aquatic environment is lacking because it is difficult to obtain chemical *in situ* information with interface selectivity. Here we apply interface selective sum frequency (SF) vibrational spectroscopy to study the speciation of the (001) surface of sapphire (α -Al₂O₃) under water between pH 4 and 12. The technique allows us also to measure the absolute polar orientation of the water molecules adjacent to the mineral surface. The inversion of the molecules' polar orientation upon the alteration of the pH indicates the point of zero charge (pzc). We use sapphire as a simple model for natural clay minerals and related iron phases. The data are required in order to reliably predict the migration of actinide ions in the aquifer. These studies are an essential part of our research on the safety of repositories for nuclear waste.

In the O-H stretch region of the infrared spectrum between 2800 and 4000 cm⁻¹, we observe a surprisingly large number of 7 SF bands in total. Two of them are due to the polar ordered water film near the mineral surface which is well known from various aquatic interfaces. At high pH, we observe the water dipoles to point into the direction of the mineral surface. This is consistent with a negative surface charge. The dipoles' orientation is reversed near pH 6 indicating that we have crossed the pzc. The other 5 bands originate from up to 5 different aluminol species or from specifically bound water molecules. The main peak with the SF intensity maximum at 3690 cm⁻¹, we attribute to an OH group bridging two aluminium atoms. A peak at 3450 cm⁻¹ corresponds to a species with its O-H bond almost in the surface plane. Its SF intensity increases considerably below pH 6 indicating a strong increase of its concentration. At pH 4, we additionally observe a water species whose dipole points into the direction of the mineral surface. The oxygens of the in-plane OH species might act as hydrogen bond acceptors for these water molecules.

Gas adsorption microcalorimetry: Probing energetics of oxide surfaces

S.V. USHAKOV, N. DALALO AND A. NAVROTSKY

Thermochemistry Facility and NEAT ORU, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA (anavrotsky@ucdavis.edu)

There is a paucity of data on direct measurement of energies of gas adsorption on mineral surfaces. Two new approaches for volumetric static and pulse dynamic adsorption microcalorimetry were developed at the UC Davis Thermochemistry Facility. The dynamic technique for chemisorption microcalorimetry implemented based on Netzsch 449 instrument, providing differential scanning calorimetry (DSC) and thermogravimetry (TG) capabilities. Pulses of the adsorbate are introduced in a gas constantly flowing through the sample chamber. The adsorbed amount is recorded as a sample weight change. Heat of adsorption is derived from the DSC trace.

The instrumental design for static volumetric adsorption microcalorimetry consists of a modified commercial surface area analyzer (Micromeritics ASAP 2020) and a Calvet-type twin microcalorimeter (Setaram DSC 111). The surface area analyzer provides automated dosing and measurement of adsorbed amounts of water vapor or gas of interest. The microcalorimeter records corresponding heat effects. The sensitivity of the instruments enables measurements on the samples with total surface area less than 5 m².

Examples of application of both methods will be given. For monoclinic zirconia and hafnia samples annealed at 800 °C in vacuum, heats of water adsorption on most energetic sites were measured using volumetric adsorption technique and found to be in the range -274 to -291 kJ per mole of water. For tetragonal ZrO₂ and HfO₂ treated in the same conditions, the initial heat values were measured as -156 and -119 kJ per mole of water. Smaller heats of water adsorption on the surface of tetragonal phases of ZrO₂ and HfO₂ support arguments on the thermodynamic nature of their stabilization at ambient by a surface energy term. Complementing oxide-melt solution calorimetry techniques with adsorption microcalorimetry data allows for experimental measurements of surface energies.

The surfaces of iron-bearing minerals: Key reactive substrates in Earth systems

D.J. VAUGHAN, R.S. CUTTING AND P.L. WINCOTT

School of Earth, Atmospheric and Environmental Sciences, and Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester M13 9PL, UK
(David.Vaughan@manchester.ac.uk)

As the most geochemically abundant of the transition metals, iron occupies a unique position in Earth systems science. The richness and diversity of the mineral chemistry of iron is particularly well illustrated by the binary oxides/hydroxides and the sulfides of this metal, phases which also span a key redox boundary in much of the near-surface sedimentary environment.

Recent experimental studies in Manchester have been concerned with exploring the nature of iron oxide and sulfide mineral surfaces at the molecular scale, using both imaging and spectroscopic methods. The surface structures and reactivities of well crystallized phases such as magnetite, haematite and pyrrhotite have been clarified by careful scanning probe studies in UHV; this has included direct observation of reactions with oxygen, water and simple organic molecules such as formic acid, pyridine and carbon tetrachloride. On the other hand, reactions at the mineral – aqueous solution interface of very fine particle oxyhydroxides (such as goethite) and sulfides (such as mackinawite) with a wide range of dissolved metals have been studied more indirectly, using techniques such as X-ray absorption and X-ray photoelectron spectroscopies. Systems investigated have included those involving reaction with certain transition metals (eg Mn, Co, Ni, Cu), heavy metals (eg Cd, Hg) and nuclear metals (eg U, Np). What emerges from these studies is a diversity of behaviour, with phenomena including surface complexation, partial and total replacement reactions, and precipitation (in some cases involving redox processes).

This behavioural diversity is further extended when the reactions entail the activities of micro-organisms, and one goal of current work is to understand the mechanisms of the *direct* reactions between the solid mineral surface and microbes such as *Geobacter*. Examples of the surface chemistry of iron-bearing minerals will be presented, and the current state of knowledge discussed.

Structure and reactivity of hydroxylated hematite surfaces: Application of surface x-ray diffraction and spectroscopy

T.P. TRAINOR¹, P.J. ENG², A.M. CHAKA³, C.S.LO³,
K. TANWAR¹, S.K. GHOSE², G.E. BROWN JR.⁴,
J.G. CATALANO⁵, G.A. WAYCHUNAS⁶ AND
A.S. TEMPELTON⁷

¹Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, AK 99775 (fftpt@uaf.edu, ftkjt@uaf.edu)

²Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637 (eng@cars.uchicago.edu, ghose@cars.uchicago.edu)

³National Institute of Standards and Technology, Gaithersburg, MD 20899 (anne.chaka@nist.gov, cynthia.lo@nist.gov)

⁴Dept. of Geological and Env. Sciences, Stanford University, Stanford, CA 94305 (gordon@pangea.stanford.edu)

⁵Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439 (catalano@anl.gov)

⁶Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (gawaychunas@lbl.gov)

⁷Marine Biology Division, Scripps Inst. of Oceanography, San Diego, CA 92093 (atempleton@ucsd.edu)

Chemical reactions at the mineral-water interface play a critical role dictating the environmental fate of aqueous compounds. In order to develop a detailed molecular scale understanding of the structure-reactivity relationship of environmental interfaces it is necessary to obtain structural information localized to mineral-fluid interfaces under realistic chemical and physical conditions. We will discuss the application of synchrotron based x-ray scattering and spectroscopic techniques to the analysis of mineral surface structure and reactivity. Specifically, we will focus on recent results of the structure of the hydroxylated hematite (0001) and (1-102) surfaces, and the crystal face specific reactivity with respect to aqueous Pb(II). These results will be compared with previous work on iso-structural α -Al₂O₃ surfaces and *ab initio* computational studies of surface structure and reactivity.

Hematite (012) surfaces and interaction with water by molecular modeling

JIANWEI WANG AND JAMES R. RUSTAD

Department of Geology, University of California at Davis, Davis, CA 95616, USA (wang@geology.ucdavis.edu, rustad@geology.ucdavis.edu)

Interaction between water and solid surfaces can substantially affect the properties of both phases, including structure and dynamics of the near surface water and reactivity and functionality of the substrate surface. This interaction is largely controlled by the surface structures, compositions, and surface charge distributions and surface redox environment, that vary widely among minerals and aqueous conditions. Hematite, the most stable oxide of iron under Earth's surface environment, is abundant in natural environment. Two oxidation states of hematite (012) surfaces, (1×1) – oxidized state and (2×1) – reduced state, are an ideal model systems to elucidate mineral surface redox reaction, and the fundamental understanding of their interaction with water will provide insight on the such processes as surface induced / mediated redox reaction and the control of multi-valence ion minerals on redox condition of natural aqueous system, which has significant impacts on human being's living environment.

The present work concerns the characterizations of the structures of hematite (012) surfaces and the effect of the surface structure and oxidation state on water adsorption, e.g., surface Fe²⁺ and Fe³⁺ distributions and surface relaxation/reconstruction on the nature, structure and energetics of water adsorption. Energy minimizations, molecular dynamics simulations and *ab initio* calculation were performed on the (1×1) and (2×1) surfaces of hematite (012). Our results suggest that at oxidized state, the bulk terminated surface experiences significant surface relaxation but no reconstruction, consistent with the previous studies. However, at reduced state, more stable configuration was found that half of the reduced Fe²⁺ ions stay in the octahedrons in the surface octahedral layer and the other reduced Fe²⁺ ions are in the second layer from the surface, indicating electron transfer from the surface layer into deeper layer from the surface. The resulting structure is incomparable to the structure of neither hematite nor magnetite. Both chemically and physically adsorbed water are observed in the water adsorption simulations. The adsorption behavior on both surfaces is qualitatively consistent with experimental observations.

Interaction of cytochromes with oxide surfaces: Adsorption-induced conformation change?

C.M. EGGLESTON¹, N. KHARE² AND D. LOVELACE³

Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming (¹carrick@uwyo.edu, ²nidhi@uwyo.edu, ³geodave@uwyo.edu)

The interaction of redox metalloproteins such as cytochromes with oxides is relevant to certain biosensors, to sensitized photovoltaics, the use of cytochromes as environmental redox catalysts, and the respiration of certain bacteria. Here, we use mitochondrial cytochrome c (Mcc) as a model because it is well studied (with a wealth of comparative background information) and is known to adopt conformational states with redox properties similar to the native states of key bacterial cytochromes. A key question is that of adsorption-induced conformation change, because such change can alter the redox potentials of the cytochrome and thereby induce electron transfer.

The pH- and ionic strength-dependence of Mcc sorption on hematite is consistent with mainly electrostatic interaction. A narrow peak in adsorption occurs between pH 8.5 and pH 10, which are the point of zero charge of hematite and the isoelectric point of Mcc respectively. Adsorption is enhanced on the low pH side of this peak in the presence of aqueous phosphate. Sorption declines with ionic strength. However, adsorption is non-zero over a broader pH range, which suggests that other interactions play a role as well.

Contact-mode versus AC-mode AFM imaging shows that Mcc is loosely bound to the hematite surface, and electrochemical STM of Mcc on graphite reveals a possible electrochemical resonance peak along step edges (but not from terraces) that is consistent with native Mcc. Direct electrochemistry of Mcc on hematite and SnO₂ electrodes is consistent with native-state protein, but XANES/EXAFS data suggest the adsorbed protein is significantly different from the native state and similar to states induced by denaturants. Possibly the oxide surface becomes “coated” with denatured protein that then insulates it from direct interaction with further protein.

Sorption of proteins and other organic molecules can be studied using optical second harmonic generation (SHG), which will be demonstrated and discussed here. In summary, our results suggest that there are some subtle structural rearrangements that occur upon Mcc adsorption to oxide surfaces, and these can have a direct effect upon the electron transfer properties of Mcc.

Surface reactivity, bacteria, and metal isotope fractionation

SUSAN L. BRANTLEY¹, JE-HUN JANG¹,
LAURA LIERMANN¹, MING TIEN², SHANE RUEBUSH²
AND RYAN MATHUR³

¹Department of Geosciences, Pennsylvania State University, University Park, PA 16801, USA (brantley@essc.psu.edu)

²Department of Biochemistry and Molecular Biology, Pennsylvania State University, University Park, PA 16801, USA

³Department of Geology, Juniata College, Huntingdon, PA, USA

The use of isotopes to investigate mechanisms of mineral reaction, well established for the light isotopes, has only recently been attempted with transition metal isotopes. Isotopic fractionation during mineral-water reaction could elucidate complex mineral reactions under abiotic and biotic conditions. For example, during adsorption of Fe(II) onto goethite under anaerobic and abiotic conditions, isotopic fractionation occurs such that sorbed Fe becomes isotopically heavy. The addition of a siderophore affects the fractionation, perhaps suggesting that the siderophore effectively blocks the complexation of ⁵⁶Fe(II) with surface sites on goethite. *In vitro* reduction experiments show that the membrane fraction of an iron-reducing bacterium could also have a similar effect as the siderophore, perhaps indicating complexation reactions between Fe(II) and membrane fractions. However, isotopic mass balance suggests that sorption of Fe(II) at the surface is accompanied by increasing incorporation of structural Fe within the goethite. We are investigating how the time-dependent incorporation of Fe at the mineral surface affects metal isotope fractionation in order to clarify the processes of aging of goethite in aqueous solutions with and without the presence of dissimilatory iron-reducing bacteria. Such isotopic investigations provide a new probe to elucidate mineral-water-bacteria reactions.

Defect distribution and dissolution morphologies on low-index surfaces of α -quartz.

SVETLANA. V. YANINA¹, KEVIN M. ROSSO¹
AND PAUL MEAKIN²

¹Pacific Northwest National Laboratory, P.O. Box 999, MSIN
K8-96, Richland, WA 99353, USA

(svetlana.yanina@pnl.gov, kevin.rosso@pnl.gov)

³Idaho National Laboratory, P.O. Box 1625, Mail Stop 2025,
Idaho Falls ID 83415-2025, USA (meakp@inel.gov)

Dissolution of mineral surfaces is a ubiquitous geochemical process. The morphology of dissolving mineral surfaces is often complex because of the influence of defects. Common mechanisms of surface dissolution include the etching of extended defects (pitting), and step-wise dissolution. The contribution of a given dissolution mechanism to surface morphology depends on the distribution of defects (such as dislocations and pores) and steps on the surface in question. The contributions of different kinds of defects can interact and produce a topography that is difficult to characterize quantitatively using standard methods. The present work aims to 1) analyze the morphological differences that arise from changes in the distribution of emerging defects on the prismatic (100) and rhombohedral (101) surfaces of α -quartz, and 2) beyond standard analyses, apply scaling concepts and wavelet analysis to the characterization of such surfaces.

The dissolution of the prismatic quartz face in 0.01 M KOH solution at 400-500 K is dominated by pits centered on dislocation sites. The recurrent emergence and pitting of dislocations produced an increasingly rough surface morphology with time on all length scales observed (1 – 90 microns). Dissolution on the rhombohedral face proceeds mostly through step-wise dissolution on the small scale (1-10 microns). Only on large length scales (50-90 microns) did extended defects contribute to the surface morphology. As a result, the roughness of the rhombohedral surface stayed stable on the $\leq 1 \mu\text{m}$ scale throughout the reaction, and reached its saturation value on the 10-90 μm scale within 60 hours of the reaction.

Fast kinetic Monte Carlo models for defect controlled dissolution of multiple etch pits

PAUL MEAKIN¹, KEVIN M. ROSSO²
AND SVETLANA YANINA²

¹Idaho National Laboratory (meakp@inel.gov)

²Pacific Northwest National Laboratory

(Kevin.rosso@pnl.gov, svetlana.yanina@pnl.gov)

Kinetic Monte Carlo models have been developed to simulate the dissolution of etch pits under the control of multiple dislocations and point defects. Simulations like that shown in figure 1 required the development of fast algorithms for large systems. The computer models are being used in conjunction with laboratory experiments to develop a better understanding of the formation of geometrically complex surfaces during dissolution.

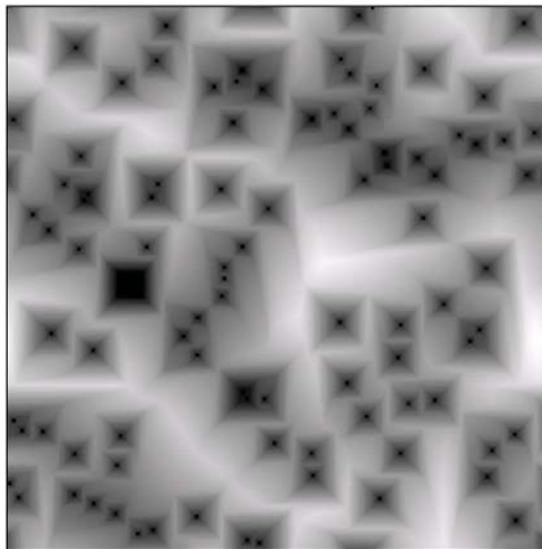


Figure 1: Cubic lattice model simulation of the dissolution of a mineral surface controlled by 100 screw dislocations in an area of 2048×2048 lattice units.

Classical nucleation theory predicts dissolution kinetics of silica

P.M. DOVE¹, N. HAN¹ AND J.J. DE YOREO²

¹Dept. of Geosciences, Virginia Tech, USA (dove@vt.edu
nhan@vt.edu)

²Chem. and Mat. Sciences LLNL, USA (deyoreo1@llnl.gov)

Issue

Silicate mineral weathering has a primary control on biogeochemical cycles of elements through earth systems. This has motivated studies of dissolution for more than 50 years. Current rate 'laws' are largely empirical, sometimes with apparent, serious inconsistencies. We show that dissolution of silica and silicate minerals can be understood across broad conditions through the same nucleation rate theory that was originally developed for crystal growth. This theory should, in principle, also apply to dissolution but, before now, has never been tested.

Methods

Kinetic measurements were conducted at 200°C using quartz sand (Destin, FL) using established flow-through reactor methods for measuring H₄SiO₄ production rate at steady state. Undersaturated solutions were prepared with and without reagent grade NaCl or CaCl₂•2H₂O and additions of silicic acid. All solutions had circumneutral pH and calculated pHT₂₀₀ = 5.7.

Parallel experiments exposed natural (100) surfaces of a euhedral quartz crystal to four experimental conditions that, according to theory, should give distinct dissolution mechanisms. Samples were restrained using Ti screen. Durations of each treatment were determined from measured rates to calculate reaction time necessary to give equal silica production at 200°C. Thus, etching times ranged from 28 days to four hours. Resulting nanoscale structures were examined under a drop of water using atomic force microscopy.

Findings

By generalizing nucleation theory across the potential energy continuum of growth to dissolution, we present a quantitative and mechanistic model that predicts how quartz dissolution processes change with increasing undersaturation from simple step edge retreat, to dislocation and defect-driven pit nucleation. We further show that the origin of the so-called salt effect that was recognized almost 100 years ago arises from increases in surface energy to activate dissolution by two-dimensional nucleation of vacancy islands, to greatly increase site density. This process has not been heretofore recognized as possible for oxide or silicate minerals. Nucleation rate theory also predicts the dissolution kinetics of dominant aluminosilicates, kaolinite and K-feldspar to resolve controversial discrepancies in 80 & 150°C data reported for kaolinite. The differences naturally arise from temperature-activated changes in the dominant dissolution mechanism. Nucleation rate theory may be the missing link to understanding the dissolution-growth continuum.

Hydration and dissolution of nano-particulate silicate surfaces

Z. DU¹ AND N.H. DE LEEUW^{1,2}

¹School of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, UK
(z.du@mail.cryst.bbk.ac.uk)

²Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
(n.h.deleeuw@ucl.ac.uk)

A range of complementary computer modelling techniques has been employed to study a series of silicate/water interfaces. Firstly, density functional theory (DFT) calculations as well as interatomic potential-based simulations have been employed to study the adsorption of water at two α -quartz (0001) surfaces, where the different methods are found to be in good agreement, both as to modes and energies of adsorption. When under-coordinated silicon and oxygen atoms are present at the surface, water molecules adsorb dissociatively at the surface, thereby annihilating dangling bonds by the formation of surface hydroxy groups. However, when the surface species are linked by Si-O-Si bridges and fully coordinated, water adsorbs associatively, releasing approximately 40 kJ mol⁻¹. The comparison study shows that the potential model for hydrated silica performs sufficiently well to be suitable for use in our further simulations of the hydration of a silicate nano-tube. Results of these calculations show that the side of the nano-tube is relatively resistant against dissociative chemisorption and silicon dissolution, but that the end of the nano-tube is highly reactive towards water and amenable to dissolution. Secondly, classical molecular dynamics simulations have been carried out to investigate the dissolution of the same quartz (0001) surfaces in a more realistic, liquid water environment. Preliminary results suggest that on thermodynamic grounds the complete dissolution of silicon atoms from the quartz surfaces in liquid water is unlikely to occur.

Tribochemical studies at the nanometer scale: Synergisms of mechanical and chemical forces

TOM DICKINSON

Washington State University, Dept. of Physics (jtd@wsu.edu)

Bond breaking at surfaces due to stimuli such as exposure of materials to radiation, mechanical stress, or chemical agents are well established. The forces and potentials available to break and reestablish bonds between ions, atoms, and molecules becomes greatly expanded when we consider combining stimuli. Our efforts on combining (mechanical + chemical) or (mechanical+radiative) stimulation aim at understanding the resulting synergisms in, for example, dissolution and/or deposition of material. Here we determine the kinetics of chemical mechanical wear (or polishing) with a single asperity (the tip of an Atomic Force Microscope) on substrates of single crystals, amorphous materials such as silicate glasses, and on polycrystalline oxides controlled chemical media. We find that although the mechanics are relatively straight forward to model using Hertzian mechanics, the *dependence* on the applied normal force (F_N), the applied stress (σ), the solution composition, the solution temperature (T), the duration time of the wear experiment (t), and the relative velocity of the AFM tip and substrate(v) can be complex. In almost all cases studied, we find that simultaneous to modification of the substrate we experience wear of the tip. By using a tip only once for the formation of each observed wear pattern on the substrate for a given set of parameters (e.g., F_N , σ , T, t, and v) and imaging the tip before and after, we are able to model the instantaneous stress (which is dropping) as a function of time during the wearing process. This allows us to unambiguously determine the stress dependence of single asperity wear as well as stress induced dissolution. The latter can also be studied in simple static loading (no sliding); the measured rates are found to be enhanced considerably in the presence of atomic steps on the surface. The minerals of interest include calcite and brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). We also show that at supersaturation, we can induce crystal growth at rates 10-20 times higher than spontaneous growth with the AFM tip. Evidence is presented to show that the crystallinity of the growth is considerably better for the tip-induced growth compared to spontaneous growth. Finally, we show that combined mechanical and chemical stimuli greatly increase the rate of removal of strongly adhering particles on flat substrates modeled by an environmental crack growth mechanism.

Interaction of Cr, As, and U-containing pollutants with mineral-water interfaces studied by second harmonic and sum frequency generation

HIND A. AL-ABADLEH, AMANDA L. MIFFLIN,
CHRISTOPHER T. KONEK, MICHAEL J. MUSORRAFITI,
ANDREA B. VOGES AND FRANZ M. GEIGER

Northwestern University Department of Chemistry, Evanston,
IL, 60208, USA (geigerf@chem.northwestern.edu)

It is now known that mineral-water interfaces can control the transport and chemical transformation of many groundwater pollutants. We present surface-specific, submonolayer-sensitive, real-time second harmonic generation (SHG) studies for monitoring the inorganic priority groundwater pollutants Cr(VI) and U(VI), as well as the organic arsenical Roxarsone, a poultry-feed additive, at silica-water interfaces. Thermodynamic, kinetic, and spectroscopic data are obtained using environmentally representative solute concentrations, and can be used to improve the reliability of existing pollutant transport models. Finally, vibrational sum frequency studies are presented that characterize geochemically important organic functional groups at mineral surfaces. These studies show that nonlinear optical spectroscopies yield important molecular-level information that is complementary to x-ray based techniques, and that they are well-suited for studying heterogeneous processes at mineral-water interfaces in real time, with high sensitivity, and under environmentally representative pH, temperature and concentration conditions.

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***In situ* x-ray reflectivity study of the mica-fulvic acid interface**

S.S. LEE¹, K.L. NAGY¹, P. FENTER²
AND N.C. STURCHIO¹

¹Dept. of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL 60607, USA

(slee28@uic.edu, klnagy@uic.edu, sturchio@uic.edu)

²Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439, USA (fenter@anl.gov)

Mineral-organic interface structures are important in controlling physical and chemical properties of soils. The presence of bridging cations is thought to affect this structure because many soil organics typically show amphoteric behaviour. In this study, in-situ specular X-ray reflectivity measurements of the muscovite-soil fulvic acid interface were obtained with high-brilliance synchrotron radiation (Advanced Photon Source; BESSRC 11-ID) to construct an adsorption model of the fulvic acid on the mica surface with Ångström-scale precision. Experiments were conducted with ASTM-V1 grade muscovite, 100 ppm Elliott Soil Fulvic Acid II (IHSS), and 0.005 m BaCl₂ solution.

It was necessary to choose an adequate structural model for the soil fulvic acid, which is composed of polymeric rather than simple molecules. The model selected was a series of Gaussian peaks whose heights and widths were allowed to be varied arbitrarily. The best-fit model of the derived interfacial electron density profile in a 0.005 m BaCl₂ solution showed two discrete peaks, the first more electron-dense than the second, at 1.90 ± 0.04 Å and 2.91 ± 0.08 Å above the mica surface. These peaks correspond to the positions of barium and/or adsorbed water in ditrigonal and basal oxygen surface sites. The best-fit model of the mica-100 ppm fulvic acid data consisted of a discrete peak 2.62 ± 0.09 Å above the mica surface, with other weaker changes in the electron density extending away from the surface. We interpret these changes as due to the formation of a ~ 10 Å thick fulvic acid layer whose thickness is imprecise because of relatively diffuse film interfaces and poor density contrast with the water layer. In a 0.005 m BaCl₂-100 ppm fulvic acid solution, the electron density peaks nearest the surface matched those in the BaCl₂ solution. The model also suggests a more compact fulvic acid layer, approximately 7.4 Å thick, with sharper boundaries as compared to the model of the fulvic acid layer alone. The model provides insight into the role that barium plays as a bridging cation which may include causing the adsorbed fulvic acid layer to become more condensed.

***In situ* AFM study of vermiculite and hydrobiotite interface reactions**

KIRILL ALDUSHIN¹, GUNTRAM JORDAN¹
AND WOLFGANG W. SCHMAHL²

¹Institut für Geol., Mineral. & Geophys., Ruhr-Uni-Bochum, Germany (k_aldushin@hotmail.com)

²Dept. für Geo- und Umweltwissenschaften, Sektion Kristallographie, Theresienstr. 41, 80333 München, Germany

In situ AFM studies show that the alteration of vermiculite and hydrobiotite in aqueous solutions under acidic conditions comprises of several stages: a) uniform crystalline swelling; b) formation of hillocks and dendritic bulges (Fig.1); c) dissolution via etch pit formation; d) decomposition of bulges; e) depolymerization of silicate layers. While the first step is likely caused by hydration of insufficiently hydrated interlayer cations, the formation of hillocks and bulges may be explained by anisotropic osmotic swelling and delamination of silicate sheets. The formation of bulges is not limited to the surface, but also affects deeper interlayers. The three latter stages of alteration (c-e) are slow under ambient conditions, but can be readily observed at $T = 50 - 125$ °C.

Comparison to other phyllosilicates shows that under acidic conditions vermiculite and hydrobiotite behave very similar to chlorite, but differ to phlogopite and apophyllite (Aldushin et al., 2004a,b). The results provide new details about the kinetics and mechanisms of swelling as a response of sheet silicates to aqueous solutions and stress the reactivity of basal surfaces of phyllosilicates.

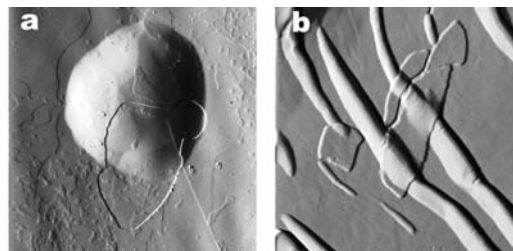


Figure 1. Hillock (a; scan field 6×6 μm^2) and bulges (b; scan field 1.5×1.5 μm^2) on the vermiculite surface.

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“Hydration” of rhyolitic glasses: Comparison between high- and low-temperature processes

LAWRENCE M. ANOVITZ^{1,2}, LEE R. RICIPUTI³,
DAVID R. COLE² AND MOSTAFA FAYEK⁴

¹Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, Tennessee 37996, USA

²Chemical Sciences Division, MS 6110, P.O. Box 2008, Bldg. 4500S, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110, USA

³Chemical Sciences Division, MS 6375, P.O. Box 2008, Bldg. 4500S, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6375, USA

⁴Chemical Sciences Division, MS 6131, P.O. Box 2008, Bldg. 4500S, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6131, USA

While much is known about the interaction between water and rhyolitic glasses and melts at temperatures above the glass transition, the nature of this interaction at lower temperatures is more obscure. Comparisons between high- and low-temperature diffusive studies suggest that several factors play an important role under lower-temperature conditions that are not significant at higher temperatures. Surface concentrations, which equilibrate quickly at high temperature, change far more slowly as temperatures decrease, and may not equilibrate at room temperature for hundreds or thousands of years. In addition, while diffusion coefficients are compositionally dependent under all known conditions, at lower temperatures they appear to be time-dependent as well. Both of these differences may be due to the inability of “self-stress”, caused by the in-diffusing species, to relax at lower temperatures. Preliminary calculations suggest that the magnitude of stress involved may be very high. On the microstructural scale, extrapolations of high-temperature FTIR data to lower temperatures suggests there should be little or no hydroxyl present in glasses “hydrated” at low temperatures, but low-temperature FTIR data suggest that hydroxyl is present. SIMS analysis of H and O, however, clearly suggest that only the hydrogen from water enters the glass at lower temperatures, not oxygen. There are no data available to directly test this possibility at higher temperatures, but comparisons of hydrogen and deuterium diffusion rates suggest that it may occur at higher temperatures as well. Although FTIR data suggest that hydroxyl groups and molecular water are present, these may represent a time-averaged bonding environment for hydrogen in the glass.

Effect of drying on mineral surface chemistry using ATR-FTIR spectroscopy and quantum mechanical modeling

MICHAEL J. BORDA¹, KRISTIAN W. PAUL¹,
JAMES D. KUIBICKI² AND DONALD L. SPARKS¹

¹Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716-1303, USA
(mborda@udel.edu)

²Department of Geosciences, the Pennsylvania State University, University Park, PA 16802, USA

Previous investigations have explored the effects of drying on the surface chemistry of minerals and soils, and shown that drying enhances acidification. This has been ascribed to the dissociation of the last few monolayers of water surrounding adjacent polarizing cations on the clay surface (Mortland and Raman, 1968.) To more directly explain impacts of drying on surface chemical phenomena, attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was employed to study drying effects in a manganese rich oxisol (Dowding et al., 2005) and the complexation of sulfate at iron oxide surfaces. In previous studies it was suggested that the formation of bi-sulfate was an artifact caused by drying wet pastes during spectroscopic studies (Persson and Lovgren, 1996) rather than as a natural process with serious implications for environmental chemistry.

This study reviews the results of Dowding et al. (2005) and shows new results for the sulfate-iron oxide system and several model minerals with differing polarizable cations. The intent is to experimentally verify the hypothesis of Mortland and Raman (1968) and to establish a correlation between the polarizability of the metal center and the ability to effect surface pH during dehydration.

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Mechanism of redox processes on iron oxides: A spectroscopic study

I.V. CHERNYSHOVA

Dept. of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA (ivcher@vt.edu)

Adsorption and reaction of sulfite, cyanide, arsenate, chromate, selenate, manganese(II), ferrous and ferric hexacyanide ions on α - and γ -Fe₂O₃, α -FeOOH, and Fe₃O₄ of similar particle size of about 100 nm and shape were studied *in situ* and *ex situ* by FTIR and X-ray photoelectron spectroscopies. For the first time, it was shown that under geochemical conditions surfaces of all the oxides contain electron-donating Fe²⁺-like defects which have extended (clustered) rather than point character. The energy level of these surface states is located in the band gap, and oxidizing species with an appropriate standard potential (arsenate, chromate, and selenate) are partially reduced upon adsorption. This effect has been previously overlooked in geochemistry.

Regularities in the kinetics and composition of the products suggest that the cathodic process of the heterogeneous oxidation includes some lattice dissolution, along with the O₂ reduction on the electron-donating defects. The relative contribution of the former process depends on 1) the complexing properties of the reagent in the reduced and/or oxidized form, 2) the ionic composition of the buffer, and 3) solubility of the oxide. The rate of the anodic counterpart of the redox reaction for both the catalytic and autocatalytic pathways increases with increasing potential of the Fermi level of the oxide. Another factor that can influence the observed rate of the heterogeneous oxidation is the adsorption rate of the reagent. Depending on the relationship between the rates of the above elementary processes, the oxidation rate of a species in a particular system can be higher as well as lower than the rate of the homogeneous oxidation.

The proposed general model of the redox processes on transition-metal semiconducting oxides was used to explain a number of inconsistencies found in the literature, in particular, those discussed by Rosso et al. (1998) about the mechanism of the heterogeneous oxidation of Mn²⁺.

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Fluoride sorption onto kaolinite: NMR spectroscopic studies

STACEY G. COCHIARA AND BRIAN L. PHILLIPS

Center for Environmental Molecular Sciences, State University of New York, Stony Brook, NY 11794, USA (brian.phillips@stonybrook.edu)

Clay minerals are important to understand many aqueous chemical reactions that occur at the Earth's surface. Kaolinite is a commonly found clay mineral in soils, as it is the main weathering product of feldspars. Methods of dissolution and sorption are especially key to understanding the mineral surface reactions at the water-mineral interface.

Kaolinite samples were used in aqueous chemistry and solid state NMR spectroscopy experiments. Fluoride sorption experiments on kaolinite were undertaken at pH 5.0, I = 10⁻³ M, 10⁻² M, and 10⁻¹ M. Fluoride reactions with mineral surfaces are relevant because of the health effects, ligand promoted dissolution, and possibly as a probe of reactive surface sites.

Both single pulse ¹⁹F Magic Angle Spinning (MAS) NMR and ¹⁹F{²⁷Al} Transfer of population in double resonance (TRAPDOR) experiments were performed on kaolinite samples to assign fluoride sorption sites. Several distinct sites were observed in the kaolinite ¹⁹F single pulse experiments, at -122, -131, and -142 ppm. Peaks at -131 and -142 ppm are similar to those observed for bayerite [1] and similarly prepared gibbsite nanoparticles, suggesting assignment to surface Al-sites. The resonance at -131 ppm is attributed to fluoride bridges, and another resonance at -142 ppm is assigned to fluoride bonded at terminal sites. In addition, sorption samples prepared in NaCl and KCl electrolytes show strong peaks near -185 ppm due to precipitation of secondary alumino-fluoride phases, whereas those prepared in CsCl do not.

¹⁹F{²⁷Al} TRAPDOR experiments confirm the assignments of fluoride sorption sites on both the kaolinite and the gibbsite surfaces. Peaks at -131 and -142 both show a TRAPDOR effect, indicating they are bound to Al, but that for the peak of -131 ppm is much stronger, consistent with assignment to Al-F-Al sites. Absence of TRAPDOR effect for the peak at -122 ppm suggests it arises from interlayer sites.

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A possible mechanism for Mn release when soils are dried

C.E. DOWDING¹, M.V. FEY¹, M.J. BORDA²
AND D.L. SPARKS²

¹Department of Soil Science, University of Stellenbosch,
South Africa (cathydowding@yahoo.co.za fey@sun.ac.za)

²Department of Plant and Soil Sciences, University of
Delaware, USA (mborda@udel.edu, dlsparks@udel.edu)

Chemical changes are known to occur when moist soils dry [1]. One of the most noticeable changes is the significant increase in exchangeable Mn in dried soils. In addition to this it has been observed that dried soils show a definite decrease in Cr oxidising capacity. It has been suggested that changes in the nature of humic substances may be responsible for these changes although how this occurs is unclear.

In the Mpumalanga Province of South Africa there are oxisols which are extremely enriched in Mn (up to 16 weight percent). Drying has a profound effect on the redox chemistry of these soils. To elucidate this drying effect we used a range of redox tests as well as surface-specific, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. With ATR-FTIR we were able to investigate the chemical changes that occur on a drying surface. These changes included a marked drop in surface pH to below 1.6 as well as a change in the sorption of oxalate from a more outer-sphere to a more inner-sphere type of surface complex. From these results and the redox analyses we suggest a mechanism for drying-induced Mn release and suppression of Cr oxidising capacity in soils which involves the formation of Mn(III)-organic complexes through a reverse disproportionation reaction induced by the combination of low pH and the stabilising effect of an organic ligand.

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Kinetics of diamond oxidation at various oxygen fugacities

Y. FEDORTCHOUK¹, E. SEMENETS² AND D. CANIL¹

¹School of Earth and Ocean sciences, University of Victoria,
Victoria, Canada (yana@uvic.ca, dcanil@uvic.ca)

²EGL Canada, Vancouver, Canada (elena@eglcanda.ca)

Variations in the oxygen fugacities (fO_2) of kimberlite magmas from the Lac de Gras kimberlite field (N.W.T., Canada) show correlation with the dissolution features of diamonds recovered from these kimberlites and their diamond content. The goal of the present experimental study is to quantitatively constrain the effect of the fO_2 on the kinetics of diamond oxidation. We used diamonds with different colours, nitrogen content and other properties to test how the properties of the diamond might influence its oxidation rate in CO₂-CO gas mixtures. Oxidation was measured by weight loss, and diameter change of the diamond.

Diamond oxidation experiments in CO₂-CO gas mixtures at 100 kPa, temperatures 1000°, 1050° and 1100°C and various log fO_2 from the range -9.6 to -16.1 ±0.1 gave a logarithmic relationship between the rate of diamond oxidation and fO_2 :

$$\log V_{\text{oxidation}} = 0.264 \log fO_2 - \text{Temperature term}$$

This function allows us to calculate the change in diamond oxidation rate with fO_2 as follows:

$$V_1/V_2 = 10^{0.264(\log fO_2(1) - \log fO_2(2))}$$

The derived relationship between the rate of diamond oxidation and fO_2 shows that the difference in 1 log unit of fO_2 will result in almost twice as fast oxidation in CO-CO₂ gas mixture. At fO_2 of the Lac de Gras kimberlites (log fO_2 = -1 log units relative to iron-wustite buffer) and 1100°C diamond of 1 mg will be oxidized in 10 hours and 0.5 carat stone in 1.5 month. At these conditions we found no effect of diamond colour (degree of plastic deformation) on the oxidation rate. The fO_2 effect on diamond oxidation in melts at high pressure and the effect of variable nitrogen content in diamonds will be studied in the future experiments.

Adsorption of Cu onto illite surfaces: The effects of ionic strength and organic acids

M.A. GONÇALVES AND J. FIGUEIRAS

Dep. Geologia/CREMINER Fac. Ciências da Universidade de Lisboa, Edifício C6, Piso 4, Campo Grande, 1749-016 Lisboa, Portugal (mgoncalves@fc.ul.pt, jmvf@fc.ul.pt)

Copper is one of the most representative transition metals in landfill leachate-derived polluted waters. Besides, these waters are heavily loaded with several groups of organic acids, namely monocarboxylic acids with 6 to 10 C atoms [1]. Previous studies [2] concluded that octanoic acid had little influence in the uptake of Cu by kaolinite surfaces.

The performed experiments used a flow-through reactor loaded with 0.5 g of the IMt-1 illite from the CMS repository, where the Cu (50–150 μM) solutions had 0.5×10^{-5} M of hexanoic acid. The pH of the solutions was 4.5, 5.5 (both 10^{-4} and 10^{-3} M IS), and 6.5 (10^{-3} M IS). A chemical equilibrium model was fitted to the experimental data of the illite suspension titration using FITEQL [3]. Surface dissociation constants were optimised, and the values obtained were $\text{p}K_{a1} = -2.94 \pm 0.11$ (surface protonation, $\equiv\text{SOH}_2^+$) and $\text{p}K_{a2} = 3.98 \pm 0.14$ (surface deprotonation, $\equiv\text{SO}^-$). Total site concentration was $5.05 \pm 0.09 \times 10^{-4}$ M.

Experiments at pH 4.5 and 5.5 reached saturation with respect to Cu adsorption, and the introduction of hexanoic acid did not show any discernible differences in the experiments. However, at pH 6.5 and higher ionic strength a slight decrease in the adsorption capacity was observed. It is presently unclear if this is an ionic strength or acid effect because ionic strength alone has a similar effect and at these pH values the amount of dissociated hexanoic acid in solution is very similar 81% (5.5) and 98% (6.5). Higher ionic strength increased the rates of Cu desorption by 65% and 57% at pH 4.5 and 5.5 respectively. It also increased the initial amount of desorbed Cu from 23% to 37% at pH 4.5, and from 6% to 29% at pH 5.5. Further experiments will use poly-functional organic acids as these are known to form more stable complexes with Cu.

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Travertine terrace growth dynamics

Ø. HAMMER AND D.K. DYSTHE

Physics of Geological Processes, University of Oslo, Postbox 1048 Blindern, 0316 Oslo, Norway
(oyvind.hammer@nhm.uio.no, d.k.dysthe@fys.uio.no)

Calcium carbonate precipitate from hydrothermal and karst-derived water often grows as terraces or carbonate rims holding pools of water. The rim height ranges from 5 mm to meters and the pool areas range from square millimeters to tens of square meters. We describe a model of the formation and growth of travertine terraces and compare the predictions with the present surface topography of an active travertine site and with vertical cuts through travertine beds.

The numerical model is based on an empirical relationship between flow rate and precipitation rate. Water flow in the evolving travertine pool geometry is calculated using a 2D fluid dynamics model. The dynamics of the system are complicated, with constant redirection of flow as the topography changes. Consequently, precipitation rate at each point fixed in space is highly variable through time. Modelling results are compared with pool shapes and pool size distribution derived from aerial photographs and laser profiling at the Troll Spring site, Svalbard. An observed minimal rim height is explained as an effect of surface tension, which is not included in the model. The model describes the emergence and coarsening of large-scale pattern from a small-scale mechanism.

The travertine quarries at Rapolano Terme, Italy, have been described in detail by Guo and Riding. We visited the quarries Cava Campo Muri and Cava la Chiusa in August 2004. The exposed walls of the quarries were up to 15 meters high and up to 100 meters long. Most walls showed flat deposits with only periodic growth of small terraces that died off again or they showed large, sloping features caused by pre-existing topography. On some walls that were cut at a favourable direction with respect to a gentle slope we could directly observe how small terraces grew in size both vertically and horizontally while the travertine was deposited. Terrace coarsening is shown to occur by rim inundation as in our numerical model and not by "step bunching" of microterraces.

An investigation on the extreme silver enrichment at tennantite surfaces in alkaline solutions: An XPS-based study

E.L. HOBSON, P. WINCOTT, D.J. VAUGHAN
AND R.A.D. PATTRICK

School of Earth, Atmospheric and Environmental Sciences
and Williamson Research Centre for Molecular
Environmental Science, University of Manchester, Oxford
Road, M13 9PL, UK

Extreme silver enrichment at the surface of the complex sulfide, tennantite ($\text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13}$), occurs in alkaline solutions, involving the development of a silver-rich sulfide species. The tennantite has a low bulk silver content of 0.3 At %, and a surface enrichment of silver is 36 times that of the bulk. The techniques of X-ray Photoelectron Spectroscopy (XPS) and Reflection Extended X-ray Absorption Fine Structure (REFLEXAFS) show the new phase to be a silver sulfide species compositionally similar to cupriferous proustite ($(\text{Cu}, \text{Ag})_3\text{AsS}_3$). Solution experiments and XPS depth profiling show the surface is most depleted in copper and zinc, and enriched in silver compared to the bulk tennantite. Dissolution of the tennantite cannot explain the diffusion and enrichment of silver from the bulk. Diffusion and enrichment have been driven by the leaching of copper which produces a metal-depleted surface, and the relative incompatibility of silver in the tennantite lattice. To account for the extreme enrichment at the surface, silver diffusion must have occurred from a depth of up to 9 nm, probably diffusing via structural weaknesses and vacancies in the tennantite lattice.

Monte Carlo simulation of surface energetic heterogeneity of goethite

LIU XIANDONG AND LU XIANCAI

State Key Laboratory of Mineral Deposit Research,
Department of Earth Sciences, Nanjing University,
Nanjing 210093, China (xcljun@nju.edu.cn)

Goethite is of abundant importance in many geochemical processes and industrial applications, where its surfaces play key roles. Molecular probe method has been proved as a powerful tool to characterize solid surface and interface property. In order to study surface energetic heterogeneity of goethite and underlying adsorption mechanisms theoretically, argon adsorption on a well-defined (010) face is simulated using Monte Carlo techniques. Grand Canonical Monte Carlo is performed to obtain Ar adsorption isotherm at 77.4 K, and Canonical Monte Carlo to determine both adsorbate-adsorbent interaction energy distribution and adsorption density distribution along z-axis. During running simulation, atom-atom interaction is approximated with the Lennard-Jones 12-6 potential. The adsorption potential minimum map above (010) is shown in Fig. 1. Fig. 2 illustrates distributions of energy and density at a representative submonolayer coverage, 0.82.

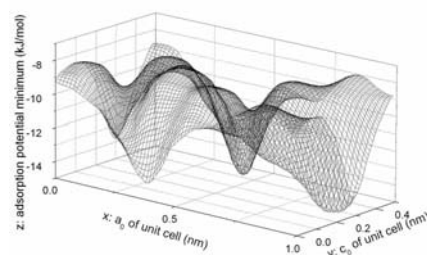


Fig. 1: Goethite adsorption potential minima above (010).

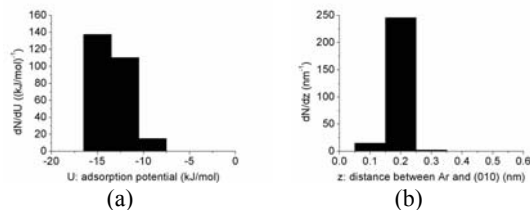


Fig. 2: (a) Energy distribution and (b) adsorption density profile, at coverage 0.82.

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Structures of the clean and hydroxylated α -Fe₂O₃ (0001) and (1 $\bar{1}$ 02) surfaces: A density functional theory investigation

C.S. LO¹, A.M. CHAKA¹ AND T.P. TRAINOR²

¹National Institute of Standards and Technology,
Gaithersburg, MD 20899, USA (cynthia.lo@nist.gov,
anne.chaka@nist.gov)

²Department of Chemistry, University of Alaska Fairbanks,
Fairbanks, AK 99775, USA (fftpt@uaf.edu)

The structure and reactivity of metal oxides such as α -Fe₂O₃ depends on several factors, including the composition of the bulk material, crystallographic orientation, local coordination of the surface atoms, and topographic arrangement of the surface functional groups. In particular, the interaction of the surfaces with water is not well understood, because the majority of experimental and theoretical data has been on the corresponding UHV-prepared or clean surfaces. These interactions play major roles in environmental processes, including contaminant sequestration, mobility, and remediation, and biogeochemical cycling of contaminants and nutrients.

We have focused our studies on investigating the structure/reactivity relationship of iron oxide surfaces under conditions encountered in environmental settings. We present density functional theory studies of the structure of clean and hydroxylated α -Fe₂O₃ (0001) and α -Fe₂O₃ (1 $\bar{1}$ 02) surfaces, and the various H and metal coordinations leading to the lowest surface free energies. We also compare our theoretical results to those from crystal truncation rod diffraction data, and discuss the differences in structure between Fe₂O₃ and Al₂O₃ that may be responsible for the differences in surface reactivity.

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Calcium oxalate surface interactions with lead

DAVID M. SINGER¹, JEFFEREY G. CATALANO²
AND GORDON E. BROWN, JR.^{1,3}

¹Department of Geological and Environmental Sciences,
Stanford University (dmsinger@stanford.edu,
gordon@pangea.stanford.edu)

²Argonne National Laboratory (catalano@anl.gov)

³Stanford Synchrotron Radiation Laboratory

Calcium Oxalate (CaOx) is a significant biomineral produced by 2/3 of all plant families, and can comprise up to 80 weight percent of bulk plant tissue. Plants and fungi can also exude oxalate, which precipitates with Ca to form CaOx within the rhizosphere and in leaf litter. While CaOx has been shown to sequester lead (Pb), the nature and stability of these interactions is unclear, which is the focus of this model system study. Bulk uptake experiments have been conducted to determine the extent of Pb uptake by CaOx, and X-ray Absorption Spectroscopy has been used to determine the nature of the uptake reaction. Batch uptake experiments indicate that the uptake of Pb by CaOx is pH-independent over the pH range of 4 to 9, but increases as a step-function above pH 9. Regardless of the initial Pb concentration, 94 to 98% of the initial Pb in solution was removed below pH 9, and nearly 100% removed above. The removal of Pb in solution also corresponded to an increase in [Ca] in solution, but constant oxalate concentrations. Pb L_{III}-EXAFS indicated that the dominant Pb phase is the same at pH 4 and 6.5, but is different at pH 11. The spectra of the uptake samples at pH 4 and 6.5, can be fit well for a Pb-oxalate crystalline phase. We have used least-squares linear combination fitting to determine what phases are present in the high pH uptake sample, which is likely a combination of Pb-oxalate and Pb-hydroxide. We conclude that aqueous Pb exchanges for Ca at the CaOx surface, forming a Pb-oxalate coating. As Pb-oxalate is less soluble than CaOx, this is potentially a significant factor in the biogeochemical cycling of Pb in surface environments where CaOx is present. The formation of metal-oxalate precipitates in plants and soils versus the formation of less stable Pb surface complexes, could retard Pb mobility.