IGPP PROGRESS REPORT

Project Title: ***Silicate Reaction Kinetics in a Major Aquifer in New Mexico (1218R)***

Principal Investigators/ Affiliations

       Chen Zhu*, Indiana University*

       George D. Guthrie*, Earth and Environmental Science Division, Los Alamos National Laboratory*

Other Investigators/ Affiliations

       Steve Chipera, Richard G. Warren, Elizabeth Keating, and David Vaniman
       Earth and Environmental Science Division, Los Alamos National Laboratory

Students/ Affiliations/ Postdocs

       Hiromi Konishi, *Indiana University*, Post-doctoral fellow
       Hui Tan, Mathew Reeder, and Peng Lu, *Indiana University*, graduate students
       Tracee Imai, undergraduate student (graduated)

Summary of Objectives, Results and Conclusions

The objective of this research project is to address a significant and long-standing problem in modern geochemistry and hydrogeology: The 2 to 5 orders of magnitude discrepancy of silicate dissolution rates between those derived from field sites and those derived from laboratory measurements. We want to test the hypothesis that field and experimental conditions are intrinsically different from those in the laboratory, in terms of biological activity, solid surface properties, solution chemistry, and transport properties. We combine the strength and expertise of the *Indiana University* (geochemical modeling, stable isotopes, field-emission gun scanning electron microscopy (FEG-SEM), availability of High-Resolution Transmission Electron Microscopy (HRTEM)) and *Los Alamos National Laboratory* (clay mineralogy, HRTEM expertise, and hydrogeological modeling) to conduct a multi-disciplinary field, microscopy, and modeling study of the kinetic rates and mechanisms of silicate reactions in a large aquifer in New Mexico. The involvement of students accomplishes both goals of a more detailed study and education of students.

In the past year, we have successfully collected clay fractions from coatings on sediment grains and performed X-ray diffraction analyses (by Drs. George Guthrie and Steve Chipera at LANL). We also started on geochemical modeling to testing the working hypothesis that feldspar dissolution is slowed down by the coupled slow clay precipitation reactions. We now have collected all necessary experimental and laboratory data, and submitted a manuscript to <u>Geochimica et Cosmochimica Acta</u>.

The SEM results show that all sediment grains have a continuous layer of coating materials, a few microns in thickness. All sediment grains, including feldspars, quartz, and titanium-iron oxides are coated with the same materials. The coating minerals appear to be a few hundreds of nanometer in size, crystalline, platy, and have chemical compositions and morphology that resemble illite-smectite. The presence of the coating materials represents a different dissolution environment from that present during the laboratory measurements, in which feldspars are ground into fine powder and thus, coatings probably do not develop. The coatings and slow kinetics of the secondary mineral precipitation may slow down the feldspar dissolution rate and cause the discrepancy between laboratory and field measured rates.

The next step is to research how to mechanistically and quantitatively explain the role of the coatings. To answer this question, we employ both an atomic scale state-of-the-art, high-resolution transmission electron microscope to examine the interface between feldspar and clayey coatings and geochemical modeling tools. Arrangements have been made for Dr. George Guthrie to use the facilities based in university. We have also started on a geochemical modeling project to explain the involvement of clay kinetics through the transition state theory. The modeling work is spearheaded by Ph.D. student Hui Tan, who is jointly supervised by Dr. Chen Zhu and George Guthrie.

The research has a new LANL relevance and perspective since its inception: feldspar dissolution kinetics plays an important role in geological carbon sequestration. This research is relevant to a number of experimental and modeling sequestration projects at LANL.

Exchange and Collaboration between University PI and Lab' PIs

In FY 2003, **Principal Investigator (Lab), Dr. George Guthrie, visited the University campus in August 2003.** Dr. Guthrie worked with and advised graduate student Hui Tan, and gave an informal presentation on research at LANL on carbon sequestration. This funded research is synergetic with the current efforts at LANL on mineral carbonation. We anticipate broader collaboration in the near future.

In the past years, Dr. Guthrie gave an excellent seminar in the Department of Geology on October 18, 2001. His seminar showcased the state-of-the-art research at Los Alamos and generated keen interest among faculty. Some contacted Dr. Guthrie for potential collaboration with the Los Alamos National Laboratory. During August 2003, Dr. Guthrie visited Pitt campus for an extended time, supervised graduate student, and started on writing a manuscript with graduate student and Chen Zhu. This project also involves Los Alamos scientists, Drs. Elizabeth Keating, David Vaniman, and David Broxton, and we have firmly established contact with each of them.

Dr. Zhu visited LANL in May 2002 for a week, and worked with Drs. Guthrie and Vaniman, and Mr. Warren.

This project has supported a number of students. Mr. Hui Tan, a graduate from the prestigious Beijing University, is enrolled in the Ph.D. program at the Indiana. LANL has world-class facilities and expertise in X-ray diffraction analyses. Mr. Tan will work

with Drs. Guthrie and Vaniman, and Mr. Warren on clay minerals that coat feldspar grains. The results will be published, and will be a part of Mr. Tan's thesis. Continued support from IGPP is crucial for them to continue this research and for Mr. Tan to complete his degree requirements. Undergraduate student, Tracee Imai performed SEM analysis of the thin sections in the summer 2002. She presented her results at GSA annual meeting in October 2002.

REPORT

I. Introduction (background and approach)

One of the fundamental problems in modern geochemistry is the lack of understanding of the rates of low-temperature silicate reactions. The large discrepancy between laboratory and field-based weathering rates of feldspars, the most abundant minerals in the Earth's crust, illustrates our poor understanding of silicate weathering systems. Field-based dissolution rates have been measured by mass balance approaches in soil profiles (summarized by White, 1995) and watersheds (summarized by Drever and Clow, 1995; and White and Blum, 1995), and the natural feldspar dissolution rates are typically several orders of magnitude slower than laboratory rates (summarized by Blum and Stillings, 1995) under similar pH conditions. The discrepancy reflects our lack of understanding of the physical and chemical processes controlling silicate dissolution kinetics in nature. There is even greater uncertainty in our understanding of rate laws for the low-temperature precipitation of secondary clays associated with feldspar dissolution, such as kaolinite and smectites (see Nagy, 1995). Establishing reliable rate laws for low-temperature weathering reactions is central to our understanding of many basic processes, including: controls on surface and groundwater quality; rates of soil development, soil fertility and the availability of inorganic nutrients; the functional relationship between silicate weathering and global climate over geologic time; and controls on dissolved elemental fluxes to the oceans.
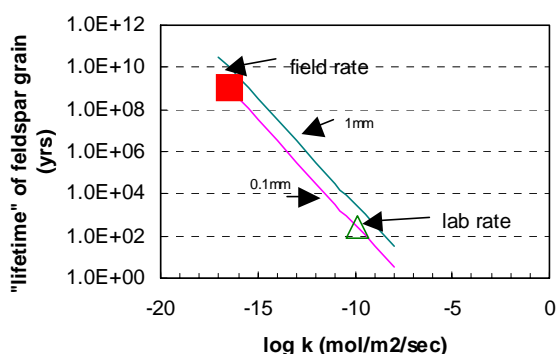

Figure 1. Calculated life span of a feldspar grain in surface environment. Following Lasaga (1998).

To illustrate the magnitude of this discrepancy, the "life span" of feldspar grains is shown in Figure 1, following Lasaga (1998). The lab rate indicates that feldspar grains of 0.1 mm in radius would be weathered away in 252 years, whereas the field-rates would lead to feldspar life time of millions of years. These calculations clearly demonstrate that to provide any meaningful interpretations of weathering reactions this discrepancy must be addressed.

The regional aquifers of the Pajarito Plateau in northern New Mexico afford an excellent opportunity to retrieve rates of feldspar reactions *in situ*. A large amount of hydrological and geochemical data has been collected in the last 30 years (Griggs, 1964;

Galusha and Blick, 1971; MacFadden, 1977; Cavazza, 1989; Waresback and Turbeville, 1990; Aldrich and Dethier, 1990; WoldeGabriel, 1991; Gabriel *et al*, in review). Recently, Keating and Warren (1999) summerized the groundwater geochemical and mineralogical data. A large amount of feldspar (20 to 40 wt%) is found in the Santa Fe Group, and petrographic observations as well as geochemical modeling show that they are altered to clay minerals. A groundwater flow model was also developed (Keating *et al*., 1998). The availbility of both groundwater and mineralogical data allows the problem to be approached from both aqueous chemistry and atomic-scale mineral alteration textures, and hence, provides an excellent opportunity to test the many hypotheses regarding feldspar dissolution kinetics.

II.   Progress during the Reporting Period

Major Findings

In the past year, we have successfully completed size fractionation, measurements of surface areas of sediment grains, and X-ray diffraction analyses. This was built upon samples collected and prepared in FY 02. Drill bits obtained from the Los Alamos National Laboratory were thin-sectioned in a commercial laboratory. The materials were first epoxy-impregnated and then polished on both sides. Scanning Electron Microscopy (SEM) was conducted on a Philips XL 30 Field Emission Gun (FEG) SEM. Back Scattered Electron imaging (BSE), Secondary Electron Imaging (SEI), and Energy Dispersive Spectroscopy (EDS) for elemental analysis, feldspar-
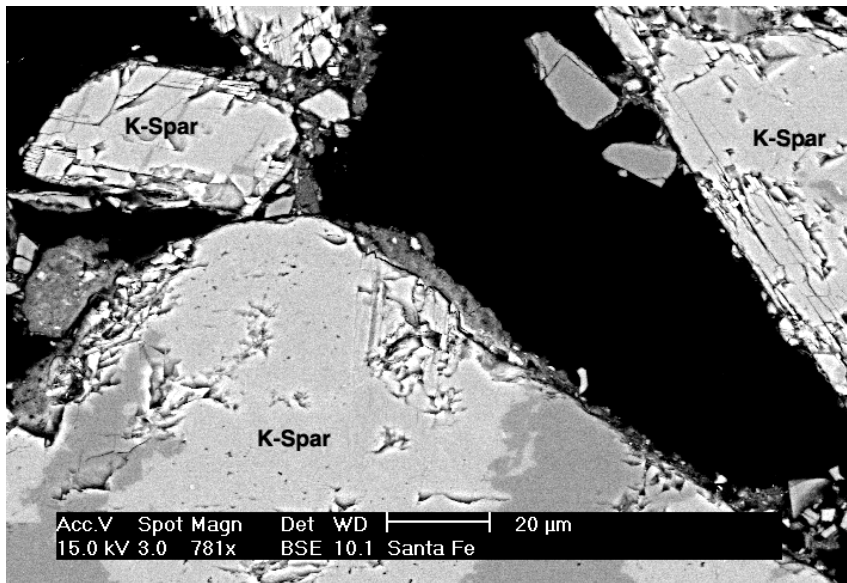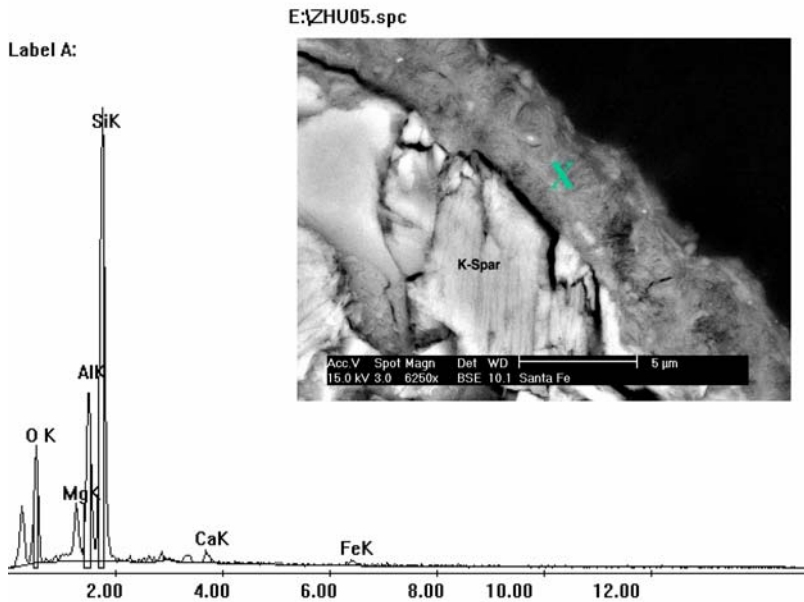

Figure 2. Electron scanning micrograph of a sandstone sample from the Santa Fe group. K-feldspars grains are coated with a layer of clayey materials. Some of the coating materials became loose during the thin sectioning.

clay interfaces were examined, using an accelerating voltage of 15 kV. A larger number of thin sections were examined using a lower resolution Personal SEM at the National Energy Technology Laboratory.

Figure 3. Enlarged electron scanning micrograph of a part of Figure 2 and EDS spectrum of the spot where the sign X indicates.

The electron microscopy results show that all sediment grains have a continuous layer of coating materials a few microns in thickness. Figure 2 shows that K-feldspar grains are coated with a layer of clayey materials of variable thickness, although during thin sectioning, some coating materials became loose. Energy dispersive spectra (Figure 3) show that the coating materials contain Si, Al, Mg, Ca, and Fe, resembling those of illite/smectite. At 100,000x magnification, the coating materials appear to be crystalline, platy and less than 100 nanometers in size (Figure 4). Note also in Figure 4, there is a gap between the coating layer and the feldspar, which is most likely caused during the thin sectioning. It, however, illustrates that clay particles do not have epitaxial growth.
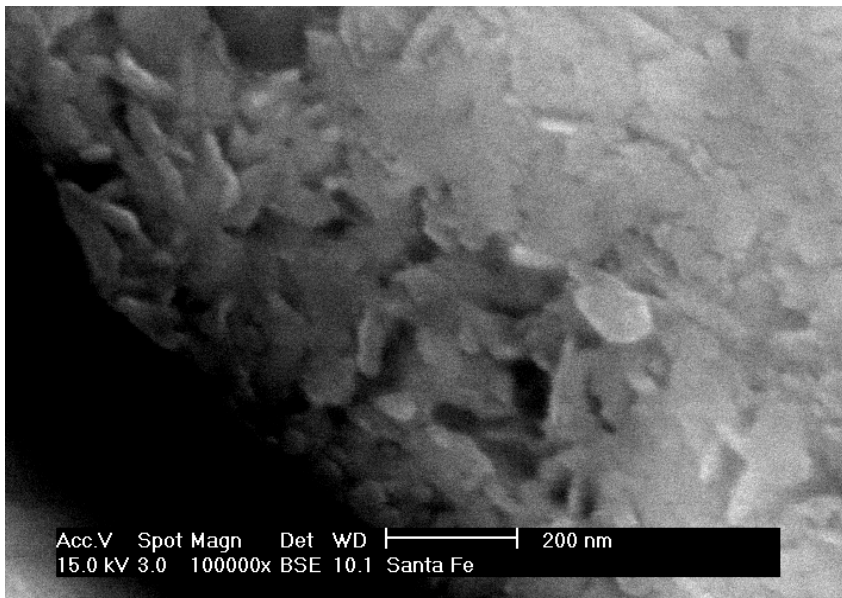

Figure 4. Enlarged view of the coating materials shown on a part of Figure 3. Trace of K-feldspar grain can still be seen at the bottom left corner. The gap between the feldspar and coating materials is believed to be caused during thin sectioning

Interestingly, not only K-feldspar grains are coated. Quartz grains, which are far more abundant than K-feldspar grains, also are coated with clayey materials. Moreover, small amounts of titanium-iron oxides were found in the samples, which also are coated with a layer of clayey materials (Figure 5). The presence of a coating on all sediment grains, regardless of grain

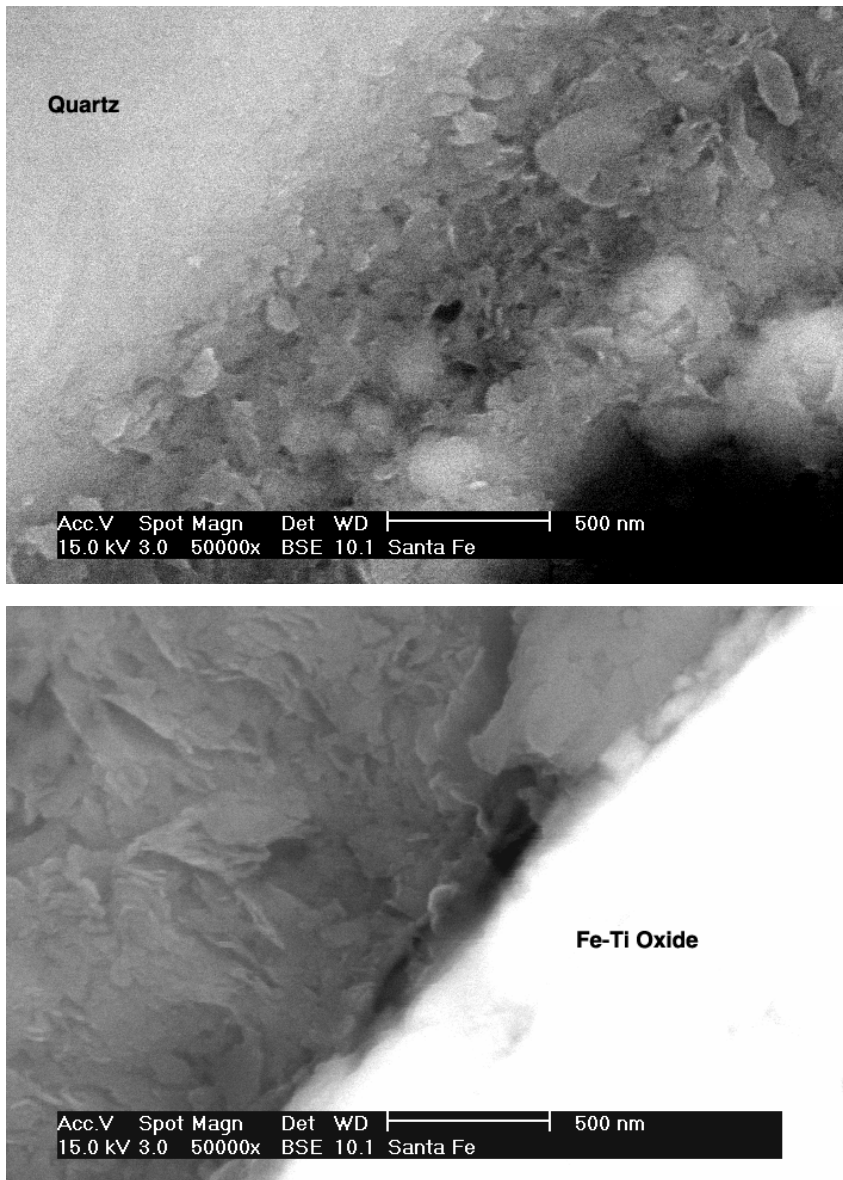compositions; raise questions about the origin of the coating formation.

Figure 5. Scanning electron micrograph showing coating on quartz (above) and titanium-iron oxides (below).

Our related electron microscopic work also revealed a highly K^+ deficient, amorphous layer on the Navajo sandstone (no lattice fringes, **Fig. 6**), which continuously covers all feldspar surfaces. The amorphous layer remains thin, having a thickness <10 nm, even after reacting for hundreds of thousands to millions of years. From the textures
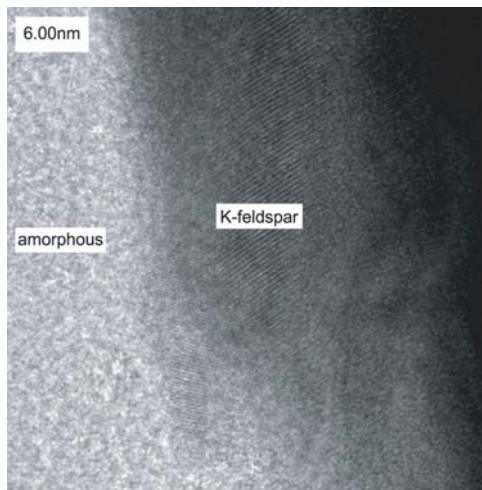
Fig. 6. High-resolution TEM images showing K-feldspar with lattice fringes at atomic resolution and a K^+ deficient amorphous layer on the feldspar surface on the left.

and K^+ signals, we interpret it as a leached layer.

A much thicker leached layer has been observed on feldspars after dissolution at acidic pH in the laboratory and in acidic soils. However, above pH 3, the presence of a true leached layer on dissolving feldspars is not well documented. It has never been observed on naturally weathered feldspars from neutral to slightly alkaline environments. Instead, previous research has suggested that a leached layer does not exist in circumneutral and basic pH solutions, and suggests that there is a different reaction mechanism in acidic or basic pH conditions. Our observations, however, indicate a similar dissolution mechanism over a wide pH range.

We are examining the feldspars from the Santa Fe group using the atomic scale microscope. The findings have significant bearings on the reaction mechanisms.

Geochemical Modeling Results

We contend that the slow precipitation of clay weathering products is such a mechanism operating in nature. If the k for clay products is significantly smaller than $k_{feldspar}$, a steady state of a low A can be maintained in a groundwater system. Our HRTEM work shows that the clay coating was formed from a dissolution-precipitation process, $feldspar \xrightarrow{k_1} aqueous\ components \xrightarrow{k_2} clays$, where k_1 and k_2 denotes feldspar and clay rate constants, respectively. For reactions in series, the slowest reaction controls the overall rate. In most laboratory experiments, the solution is dilute and undersaturated with respect to both feldspar and clays, k_1 controls the rate of feldspar rate. However, as solutes accumulate in solution and the solution is oversaturated with respect to clays, k_2 controls feldspar reaction rate. Thus, the overall rate of the feldspar dissolution along the flow path can be controlled by the slow precipitation rates of kaolinite and smectite.

This working hypothesis can be demonstrated by reaction path calculations. If feldspar initially dissolves at the laboratory rate and clay precipitates instantaneously or at local equilibrium with groundwater, feldspar dissolution rates decrease rapidly as A drops, but the system reaches equilibrium ($A = 0$) in a few years (Fig. 7). However, when $k_2 << k_1$, feldspar dissolution rate decreases rapidly due to the A effect first, as in the local equilibrium case above, but reaches a steady state where groundwater is near, but not at equilibrium with feldspar ($A \approx 0.3$ J/mol for Model 3 in Fig. 7). A k_1/k_2 ratio of 10^4 for smectite effectively reduces feldspar dissolution rate by a factor of 10^3, and a k_1/k_2

ratio of 10^6 would reduce the dissolution rate by the observed factor of 10^5. This mechanism of slow feldspar dissolution in nature is consistent with the transition state theory on the influence of chemical affinity, but with clay formation as the rate limiting process. Slower kaolinite precipitation and the rate at which the aquifer is flushed with upgradient water (advective-dispersive transport) also affect feldspar dissolution rates, which we are currently investigating. Many other factors may also contribute to the slower feldspar dissolution rates in natural systems, such as surface chemistry and inhibitors, but are more likely to be of secondary importance.
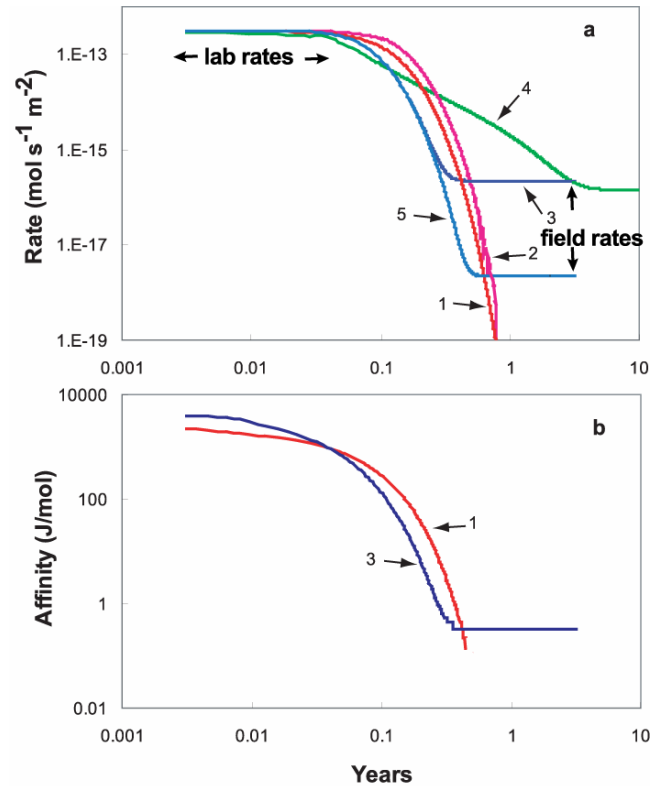

Fig. 7. Feldspar dissolution rates at different saturation states and rates of clay precipitation. Results are calculated from reaction-path models. Define effective rate constant $k^*_1 = k_1 S$. Model 1, $k^*_1 = 10^{-10.3}$ mol s^{-1} m^{-2}, $k^*_2 >> k^*_1$; 2. $k^*_2 = k^*_1$; 3. $k^*_1 = k^*_{kaolinite}$, and $k^*_{muscovite} = k^*_1 \times 10^{-4}$; 4. $k^*_{kaolinite} = k^*_1 \times 10^{-2}$, but $k^*_{muscovite} = k^*_1 \times 10^{-4}$; 5. $k^*_1 = k^*_{kaolinite}$, and $k^*_{muscovite} = k^*_1 \times 10^{-6}$. (a) Temporal evolution of feldspar dissolution rates; and (b) affinity of feldspar dissolution reactions.

B. Conclusions

The presence of the coating materials represents a different dissolution environment from that in laboratory experiments, during which feldspars are ground into fine powder and coatings probably do not develop. The coatings and slow precipitation kinetics of the secondary minerals may slow down the feldspar dissolution and cause the discrepancy between laboratory and field measured rates.

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C.   Tangible Results

The following publications acknowledge the funding from IGPP

Book

Zhu C. and Anderson G. M. (2002) *Environmental Applications of Geochemical Modeling*, Cambridge University Press, London, ISBN 0-521-80907-X; 0-521-00577-9 (pb), 304 p.

Refereed Journal Articles

Zhu, C., In situ feldspar dissolution rates in an aquifer. Geochimica et Cosmochimica Acta (in press).

Martin, S., **Zhu**, C, J. Rule, N. T. Nuhfer, R. Ford, S. Hedges, A high resolution TEM-AEM, pH titration, and modeling study of Zn^{2+} coprecipitation with ferrihydrite. *Geochimica et Cosmochimica Acta* (in press)

Zhu, C., (2003) A case against K_d-based transport model: Natural attenuation at a mill tailings site, *Computer and Geosciences*, v.29, 351-359.

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Zhu, C., and Burden, D. S. (2001) Mineralogical compositions of aquifer matrix as necessary initial conditions in reactive contaminant transport models, *Journal of Contaminant Hydrology*, v. 51 no. 3-4, 145-161.

Presentations at National Meetings

Zhu, C., A. E. Blum, S. Hedges, and C. White (2001) A tale of two rates: implications of the discrepancy between laboratory and field feldspar dissolution rates on geological carbon sequestration. *Geological Society of America Abstr. with Programs* v. 33, no. 6, A234.

Zhu, C., A.E. Blum, D.R. Veblen (2004) Feldspar dissolution rates and clay precipitation in the Navajo aquifer at Black Mesa, Arizona, USA. Proceedings form the 11thWater/Rock Interaction Conference, Saratoga Springs, New York (accepted).

Student Presentations

Imai, Tracee, and Zhu, C., 2002, Undergraduate research at the University of Pittsburgh. *Geological Society of America Abstr. with Programs*.

Manuscripts Submitted and in Preparation

Zhu, C., Guthrie, others, Clay coating on feldspar grains in saturated aquifers. *Geochimica et Cosmochimica Acta* (submitted)

Tan, Hui, Guthrie, G., Zhu, C., Reaction path modeling of coupled feldspar dissolution and clay precipitation (in prep).

D. Intangible Results
 1. New capabilities
 2. Collaborations & contacts

Dr. George Guthrie came to the campus for an extended visit in August 2003 and advised graduate student Hui Tan. The geochemical modeling work Hui Tan is performing for his thesis is closely related to the successful mineral carbonation experiments and modeling research program on-going at LANL. These two projects complement each other in understanding the complex interplay of primary mineral dissolution and secondary mineral precipitation, aqueous solution chemistry, and mineral surface properties.

Dr. Guthrie's advice to the graduate student also lends expertise that is lacking at the University: clay mineralogy. The graduate student is currently collecting mineral separate for further analysis. The interactions for graduate students with National Laboratories broaden their professional horizon. Overall, the funding and participation of LANL scientists contributed to the education and human resource development.

In fiscal year 2002, Dr. George Guthrie gave an invited seminar at the University. The seminar was well received. Some faculty members contacted Dr. Guthrie for possible, additional collaboration between Los Alamos National Laboratory and the

University. Dr. Chen Zhu visited Los Alamos National Laboratory in May 2002 to work with Dr. George Guthrie. Dr. Zhu also had conferences and discussions with Drs. Bill Carey, Rick Warren, and Vaniman.

III. Funds Received as a Result of IGPP-Sponsored Research (including granting agency)

We obtained in-kind contribution from the University in terms of faculty salary, laboratories and facilities. Because we are addressing a fundamental scientific problem, we anticipate, upon completion of the proposed research, to submit a proposal.

We will use the preliminary FEG-SEM and FEG-TEM results to prepare a proposal and submit it to the Basic Energy Sciences Program and Environmental Management Sciences Program at the U. S. Department of Energy (DOE), to investigate kinetic rates in aquifers. We also will explore funding possibilities from the Petroleum Research Fund (PRF) administrated by the American Chemical Society.

IV. Los Alamos Facilities Used for This Project

Please identify any Los Alamos facilities used (not just an acronym) and their location (Group or Division).

The X-ray diffraction facility in the EES-6 will be used for a clay mineralogy study.