PROGRESS REPORT

PROJECT TITLE: Quantifying Silica Reactivity in Subsurface Environments: An Integrated Experimental Study of Quartz and Amorphous Silica to Establish a Baseline for Glass Durability

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AWARD NUMBER: DE-FG07-01ER15123

SUBCONTRACTORS: None

GRADUATE STUDENTS: Mr. Colin Craven
Mr. Troy Lorier
Mr. Adam Wallace

UNDERGRADUATES: Ms. Christina Lopano
(now graduate student at Penn State)
Mr. David Rugh
(presently senior Geochemistry/Geoscience major)

POSTDOCTORAL SCIENTIST: Dr. Nizhou Han
Dr. Yongtian He

PROJECT OBJECTIVE and BACKGROUND:

An immediate EM science need is a reliable kinetic model that predicts long-term waste glass performance. A framework for which the kinetics of mineral-solution reactions can be used to interpret complex silicate glass properties is required to accurately describe the current and future behavior of glasses as synthetic monoliths or natural analogs. Reaction rates and mechanisms are essential elements in deciphering mineral/material reactivity trends within a compositional series or across a matrix of complex solution compositions. An essential place to start, and the goal of this research, is to quantify the reactivity of crystalline and amorphous SiO_2 phases in the complex fluids of natural systems.

Perhaps the most important motivation for quantifying SiO_2 reactivity in the fluids of subsurface environments is that an understanding of fundamental controls on the reactivity of simple Si—O bonded phases establishes baseline behavior for silica phases widely found in waste storage environments. Host rock silicate minerals dominate virtually every repository rock-water system. Further, complex silicate glasses will be the front line of defense in containing radioactive wastes in both interim and long-term storage strategies. However, we have little quantitative understanding of pure SiO_2 reactivity in the solutes of natural and perturbed groundwaters even though current EM strategy calls for dispersal of waste into silica-based glass materials. Findings will establish quantitative relationships between silica reactivity and complex solution chemistries never investigated and are presently speculative at-best. Further, we will be able to uncover an underlying principle that governs how solutes affect silica reactivity in a systematic and predictable way.

STATUS:

The new research project was initiated on February 1, 2001. We have made significant progress and all major aspects of the research activities are 1) underway or 2) findings are being prepared for publication at this time. With the completion and relocation of our new expanded laboratory in June 2002, we have two Postdoctoral Scientists, one new Ph.D. student, one undergraduate and the P.I. working on all phases of the project.

A. Interactions with Users: Tank Focus Area

The P.I., Dove, has continued to interact with TFA scientists and engineers on the problems of waste glass properties. Results of our EMSP-funded research have interfaced well with the efforts of Dr. Pete McGrail and colleagues at PNNL. Continued linkages between Dove's former EMSP-funded postdoc, Dr. Jonathan Icenhower, and his group at PNNL has further facilitated information transfer from the 'university lab to user' environment. Similarly, former EMSP-funded graduate student, Troy Lorier, now works with the Glass Chemistry group (Dr. Bill Holtzscheiter) at Westinghouse Savannah River.

B. Publications:

Lorier, T. (2000) The dissolution kinetics of quartz and amorphous silica in natural waters: A baseline for silica reactivity Georgia Institute of Technology, *M.S. Thesis*.

Craven, C.M. (2000) The effects of electrolyte solution composition on the surface charge development of silica. Georgia Institute of Technology, *M.S. Thesis*.

Karlsson, M. C.M. Craven, P.M. Dove and W.H Casey (2001) Surface charge concentrations on silica in different 1.0 M metal chloride background electrolytes and implications for dissolution rates. *Aquatic Geochemistry*, 7, p. 13-32.

P.M. Dove and C.M. Craven (submitted) Silica surface charge in alkali chloride solutions reveals roots of ionic specificity. *Geochimica Cosmochimica Acta.*

Craven, C.M. and P.M. Dove (in prep.) The effects of electrolyte solution composition on the surface charge development of silica. *Geochimica Cosmochimica Acta.*

Lorier, T. and P.M. Dove (in prep.) The dissolution kinetics of quartz and amorphous silica in natural waters: A baseline for silica reactivity. *Geochimica Cosmochimica Acta.*

Dove, P.M. and T. Lorier (in prep.) Major solute controls on silica dissolution rates. For *Nature*.

C. Awards and Recognitions:

2002 **Paul Gast Lecturer**, V.M. Goldschmidt Conference, Davos, Switzerland (P.M. Dove)
2001 **Outstanding Student Paper Award**, Hydrology Section of AGU (Mr. Colin Craven).
2000 **Fellow**, Mineralogical Society of America (P.M. Dove)
1999 **DOE Best University Research Award**, Interfacial Processes Symposium (P.M. Dove)

PLANNED ACTIVITIES:

Over the next year, we will continue activity on every aspect of the research project. During this time, Dove will also be working with Mr. Craven and Mr. Lorier to finish up several new papers that complete the publication of their MS theses. As planned from the outset, the Craven thesis was designed to ultimately produce information that would allow us to evaluate, for the first time, the roots of the kinetic data produced by Lorier and previously, PI Dove.

New postdoctoral scientist, Dr. Nizhou Han, is finishing up her experiments showing the effect of reaction affinity on rates of silica (crystalline and glassy) dissolution. After resolving some difficulties in preparing large quantities of solution that contain high concentrations of monomeric silicic acid, she was able to conduct all of the planned high Q/K solutions to obtain very high quality experimental results. These reaction affinity experiments are giving the dissolution rate of quartz and silica glass in a series of carefully selected mixed solute solutions over a range of pH and temperature. We are finding surprising differences in the rate over Q/K for the various solution compositions. They are first of their kind and these near-equilibrium solutions are of direct relevance to the types of hydrothermal solutions that will be generated in the country rock adjacent to the waste barrier system. The findings are remarkable. At this time, Dr. Han is conducting a few extra experiments to further test our unexpected findings in these unique experiments. Her final tests will be completed by the end of July (maybe August) at which time we expect to write a high quality publication.

Dr. Yongtian He joined us in April from Sam Traina's group at Ohio State. He is presently completing the background experiments and experimental design that is necessary to

conduct a carefully designed set of experiments to examine the effect of important contaminant metals on the corrosion kinetics of quartz and amorphous silica. Using the information on IIA cations from previous studies as background, Dr. He will extend our knowledge by determining the effect of important metals with a 2+ valence. These include copper, cobalt, lead, cadmium, zinc, manganese (2+) and barium. Mr. David Rugh, a senior undergraduate in Geochemistry/Geosciences at Virginia Tech is working with Dr. He and his activities will continue as a senior thesis over the next year. This is a good experience for Mr. Rugh and he is expressing interest in graduate school.

Mr. Adam Wallace is joining us in August as a Ph.D. student with a keen interest in silica chemistry. His undergraduate degree from UC Davis, Adam joins us after 18 months of work experience with the Bourcier group at Lawrence Livermore National Laboratory. Adam will be investigating silica-organic polymer interactions in corrosion and nucleation studies. His studies will be unique, in part, because we understand the importance of surface charge in controlling the behavior of these interactions. This aspect of the research will be conducted in parallel with surface investigations of selected samples/conditions. The quantitative information from his experiments will be complemented by analyses from *in situ* Atomic Force Microscopy (AFM) and *ex situ* analyses by XPS and Auger.

BUDGET DATA: Owing to the delay in establishing our new lab, the spending to-date is somewhat less than the original budget.

SPENDING PLAN FOR NEXT YEAR: Spending on the project has returned to original projections but our construction delay in 2001/2002 will inevitably lead us to request a no-cost extension to complete the project.

INFORMATION ACCESS: Please visit our web site at www.geol.vt.edu/geochem/pmd or contact dove@vt.edu