Final Report, Covering period from 1990 through 2001 with no-cost extension into 2002.

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TITLE: Reactive Fluid Flow and Applications to Diagenesis, Mineral Deposits, and Crustal Rocks

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There were no unexpended funds.

Objectives: To initiate new: modeling of coupled fluid flow and chemical reactions of geologic environments; experimental and theoretical studies of water-rock reactions; collection and interpretation of stable isotopic and geochemical field data at many spatial scales of systems involving fluid flow and reaction in environments ranging from soils to metamorphic rocks.

Project Description: Theoretical modeling of coupled fluid flow and chemical reactions, involving kinetics, has been employed to understand the differences between equilibrium, steady-state, and non-steady-state behavior of the chemical evolution of open fluid-rock systems. The numerical codes developed in this project treat multi-component, finite-rate reactions combined with advective and dispersive transport in multi-dimensions. The codes incorporate heat, mass, and isotopic transfer in both porous and fractured media. Experimental work has obtained the kinetic rate laws of pertinent silicate-water reactions and the rates of Sr release during chemical weathering. *Ab-initio* quantum mechanical techniques have been applied to obtain the kinetics and mechanisms of silicate surface reactions and isotopic exchange between water and dissolved species. Geochemical field-based studies were carried out on the Wepawaug metamorphic schist, on the Irish base-metal sediment-hosted ore system, in the Dalradian metamorphic complex in Scotland, and on weathering in the Columbia River flood basalts. The geochemical and isotopic field data, and the experimental and theoretical rate data, were used as constraints on the numerical models and to determine the length and time scales relevant to each of the field areas.

Results

Here we summarize some of the salient results that are described more fully in the references. In addition to those papers enclosed, we cite a number of dissertations which were

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supported, as well as selected conference presentations and papers in preparation that will cite support from this grant.

Our modeling of kinetically controlled mineral dissolution and precipitation revealed features never before observed. For quartz as the representative mineral phase, these include: 1) regions of downwelling oversaturated fluid experiencing heating, and regions of upwelling undersaturated fluid experiencing cooling, neither of which would be expected from models based on equilibrium, 2) significant shifts in flow direction due to precipitation/dissolution induced permeability changes, 3) the location of the basal stalk of thermal plumes rising from the heated lower boundary is inherently unstable (the core of the flow generally clogs via precipitation, whereas the edges of the stalk are dissolving, via kinetic effects), 4) Although one could expect runaway dissolution to occur in downwelling up-temperature flow, by the sequence undersaturation --> dissolution --> higher permeability --> faster flow --> greater disequilibrium, etc., runaway dissolution can be moderated by shifts in the locations of saturation state reversals. However, the runaway regime is still observed when the kinetics are faster or the grain sizes are smaller than the standard test case. We also examined the scaling behavior for how the deviation from equilibrium depends upon the kinetic rates.

Forced flux injection simulations revealed that undersaturated injection leads toward permeability homogenization along the flow direction, whereas oversaturated injection tends to increase permeability heterogeneities along the flow direction. Flow rates are significantly enhanced even between isolated high permeability zones, an effect which is even more dramatic for both closer "crack" spacing and higher permeability contrasts.

We have made significant advances in the understanding of fluid/rock interaction at high temperatures, where the fluid is a supercritical mix of water and CO_2. Our modeling effort for such mixed-volatile systems spans metamorphic reactions in contact and regional metamorphic terrains, in open and closed systems, and in one and two dimensions. Results from each of these end members illustrate that metamorphism of siliceous dolomites can exhibit significant non-equilibrium behavior when real reaction rates are considered. Only when heating rates are slow enough (a degree per 1000 years or less) and when simultaneously the system is essentially closed to fluid flux does the system behave in the way metamorphic petrologists have typically envisioned dynamical behavior as a series of equilibrium states. We have also shown that near steady state behavior can often result with a system being held far from equilibrium through a balance of fluid injection and finite reaction rates. In addition, metastable reactions often proceed and are an essential part of properly formulated kinetic models of metamorphic reactions. Carefully chosen numerical models of simple metamorphic reactions in one dimension have been used to reevaluate the water-rock ratio concept and the fluid-flux estimates typically based on equilibrium arguments. Although such flux estimates are typically within an order of magnitude of correctly modeled flow and reaction models, we have presented a more consistent model, and have shown the dangers of blindly applying the typically used flux calculations. These results should have major impact on how fluid/rock interaction is interpreted and the dominant role of open system behavior. Such results for high-temperature systems underscores the importance of considering kinetic control of fluid/rock interaction in the crust.

In the two-dimensional setting, we have found that decarbonation reactions induced by a localized heat source can lead to the dominance of either buoyancy or reaction induced flow. Not only is this result dependent upon the size of the heating body, and the rate of heating, but which regime dominates also depends critically on the effective grain size of the rock matrix. This textural dependence of the flow regime is a logical result of surface controlled kinetic reactions and the scaling behavior of permeability and grain size. Access to these flow regimes relied on an anelastic-type approximation we developed to filter out sound waves, while including the important effects of volatile production, buoyancy, and compaction. Full dispersion of the binary fluid is included in the model. In addition to significant overstepping of univariant reaction curves during prograde metamorphism, we also observed occasional understepping (with talc destruction) due to rapid influx of CO_2-rich fluids from adjacent locations. Such behavior would never occur in equilibrium-based models, but can be naturally understood with our kinetic description.

Our modeling of diffusion within grains and the interaction of grains with fluids follows the evolution of trace elements and isotopes. Our primary focus has been on kinetic isotope effects. In addition to identifying a number of time scales involved in isotopic evolution near lithologic boundaries, the theoretical model was extended to include the effect of fluid flux, recrystalization, grain size, and strongly contrasting grain-diffusion rates. In addition, we have extended the formulation to account for the effect of differing mineral densities on the mass conservation equations during recrystallization and fluid flow with compaction and fluid expulsion. Analytical solutions for isotope exchange during dissolution coupled with diffusion were developed which provided an important check for the numerical calculations.

The experimental work pioneered in our laboratories has produced several startling results on the kinetic rate laws of silicate-water reactions. Results from earlier experiments with gibbsite, kaolinite and albite suggest that the variation of the rate with saturation state is much more complex than anticipated. The presence of a surface transition in the mechanism of dissolution leads to highly nonlinear variations of the rate with ΔG_R. Such surface effects have been tentatively identified as stemming from the energetic role of dislocation defects on the surface of minerals. A new full rate law was proposed that explicitly incorporates the effect of ΔG_R, as well as that of temperature and catalysis or inhibition through the adsorption of H+, OH- and other ions. Experiments with smectite, anorthite and the zeolites analcime and clinoptilolite have confirmed the non-trivial dependence of dissolution rate on ΔG_R. The effects of pH and Al inhibition have also been studied in more detail. The development of new column experiments constitutes an important step in conducting laboratory kinetics experiments that more closely reproduce natural systems.

White light interferometry was used to measure dissolution rates of both anorthite and dolomite surfaces. Through use of an absolute reference, we could distinguish between the rates of surface retreat of most of the surface compared to etch pits. Although the surface dissolution is highly heterogeneous, the bulk rates for anorthite compared reasonably well to previous experiments, which used BET surface areas. The mean absolute rate of the dolomite surface is about 3 times slower than the rate calculated from the etch pit dissolution. Earlier batch rate data for dolomite using BET surface areas yielded rates that were at least 30-60 times faster than our directly measured mean dissolution rate for the same pH and temperature. These surface resolving dissolution experiments led to a new "stepwave" model for dissolution which accounts for the nonlinear dependence of the dissolution rate with degree of undersaturation and appears to provide a mechanistic explanation for why field observations can indicate slower dissolution rates than far-from-equilibrium laboratory studies.

The major element fluxes measured in one of the field projects have been compiled. These results and the Sr and trace element fluxes can also be found in Taylor (2000). Trace element and Sr isotope results from the field study have been published. Another set of experiments was run on biotite to determine the relationship between dissolution rates and temperature, pH and the saturation-state of the weathering solution. It was found that the dependence of biotite dissolution on pH is similar to that of other silicate minerals but that biotite weathering is much less temperature dependent than most other silicate minerals. Also, biotite dissolution rates decrease by a factor of 5 over a fairly narrow range of weathering solution saturation-states. The $^{87}Sr/^{86}Sr$ of the weathering solution is higher than that of the biotite, independent of temperature and pH. Increasing the saturation of the weathering solution, however, appeared to reduce the $^{87}Sr/^{86}Sr$ of the solution so that it was closer to the biotite ratio.

We have used *ab initio* methods to study isotope exchange reactions between dissolved species and water. Our recent emphasis was on oxygen isotope exchange mechanisms between water and orthosilicic acid, and between water and sulfate. Given the frequent use of oxygen isotope analysis to interpret processes in water/rock interaction and in atmospheric/aerosol interaction, these fundamental studies address the core assumptions of rates of exchange between species. Our work will help answer questions about the rates of exchange and whether sulfate and silicate species would tend to reflect their sources or whether rapid equilibration with water is expected.

The reaction energetics of oxygen isotope exchange between water and orthosilicic acid seem to indicate rates on the seconds to minutes timescales. The mechanism indicates that exchange is facilitated by the mobility of hydrogen ions in water. Chains of water molecules allow the effective transfer of hydrogen ions from one hydroxide group to another. The mechanism passes through a five coordinated intermediate bound by low activation energy barriers (which explains the lack of experimentally isolated dissolved five-coordinated species).

We collaborated with the Central University of Venezuela and the Venezuelan bauxite mining company, Bauxilum, to obtain data on the huge lateritic bauxite deposit in the "Los Pijiguaos" region, located in the NW edge of the Guiana Shield. The available data from this bauxite deposit consist of chemical analyses of Al2O3, SiO2, Fe2O3, TiO2 and H2O collected with a depth resolution of one meter on a 100x100 m grid. The thickness of the total weathering profile (bauxite + saprolite) is on the order of 50 m. Each point is perfectly located in a three-dimensional network. These data allow us to see the changes in composition in three dimensions and correlate the changes to topography and to flow models of the infiltrating meteoric waters. To characterize weathering properly we needed accurate modal data as well as chemical data. This fact, required us to develop an entirely new technique to obtain accurate modal analyses of samples that contained both gibbsite (Al(OH)3) and kaolinite (Al2Si2O5(OH)4). Accurate modal analyses of many bauxite samples were obtained using standard image analysis techniques on back scattered electron (BSE) images on the electron microprobe/SEM system. As it was not possible to distinguish between gibbsite (Al(OH)3) and kaolinite (Al2Si2O5(OH)4), using standard techniques, we developed a new technique involving digital image analysis of both BSE images and x-ray maps. The combination of the two types of images provided details of chemical and mineralogical composition at spatial resolution never before achieved.

The measured weathering profiles from the "Los Pijiguaos" region have an upper gibbsite-rich zone (the bauxite proper), underlain by a transition zone where both gibbsite and kaolinite are present, and a basal saprolite, with no gibbsite present. Relict quartz grains are present throughout the profiles. Simulations, using our coupled reaction flow models, both in one and two dimensions, have shown that long time scales (several millions of years) are required to produce the observed weathering profiles, and that the presence of a transition zone with both gibbsite and kaolinite is only predicted if kinetic rate laws are used. The presence of relict quartz grains is also consistent with the slow dissolution rates of quartz, even in this long time scales.

Comparison with the one dimensional model required that mechanical denudation has been active during the formation of the bauxite to explain the limited thicknesses of the weathering profiles in the field. In the two dimensional modeling the characteristics of the flow field are such that the most intense weathering and the maximum thicknesses of the weathering profiles are developed close to the vertical cliffs which limit the extension of the plateau on which the "Los Pijiguaos"' bauxite is found (most lateritic bauxites formed on plateaus are limited by steep slopes). In the field, weathering profiles become thinner upon approaching these steep slopes. Again, the effect of mechanical denudation is very important in the development of the bauxite. Physical erosion is most intense near steep slopes, preventing thick weathering sequences from developing.

Several major conclusions were drawn from the Marysville work. First and foremost, both fluid flow and the kinetics of metamorphic reactions can have a major effect in modifying isograd development. The kinetics of metamorphic reactions can also have an important effect on the fluid composition. As a result, the equilibrium T - XCO_2 curves need not be followed during metamorphic events. Of great note is that this conclusion can be reached using kinetics that are actually measurable in the laboratory. The kinetic effects, when coupled with fluid flow considerations, allow for extensive reaction to occur along the univariant T-X curves. This drastic deviation from the usual assumptions based on no-flow and infinite-kinetics leads to the conclusion that invariant points may not necessarily be the loci of identifiable isograds in the field. To properly interpret the field data, additional factors such as mineral abundances, rock texture, heating rate and reaction kinetics must be introduced.

In the Wepawaug Schist, the application of the experimental data to the kinetics of isotopic exchange of water with quartz, and the model results has already shown that fluid flow was transient in cracks (now preserved as veins). Not only was the flow transient, the isotopic composition of the fluid oscillated between values that were isotopically lighter and heavier than the surrounding host rocks.

Oxygen isotopic zonation in garnets as well as isotopic, modal and chemical profiles for individual minerals in wall rocks next to veins show that each fluid recorded in the veins infiltrated and reacted with the wall rocks. Garnets are isotopically zoned with the cores being isotopically lighter than the rims. Staurolite and kyanite throughout the profile formed late and are isotopically heavy. Quartz, biotite, and muscovite have intermediate isotopic compositions, and plagioclase is isotopically light. These results make it clear that we can no longer consider metamorphic rocks to be "closed or semi-closed" systems. Regional metamorphic rocks are, in many cases, metasomatic in origin. We can never go back to looking at whole rocks or single minerals, and we can never go back to looking at a single locality. However, the rocks do preserve some of the fluid flow history, and we can unravel that history.

A one-dimensional model of coupled advection-hydrodynamic dispersion-reaction was used to investigate processes of CO_2 release from metacarbonate beds during deep crustal (~8 kbar) prograde metamorphism. Reaction progress is driven largely by gradients in fluid composition between different rock types. Mass transfer may occur across lithologic contacts and involve substantial diffusion and/or occur through flow through metacarbonate layers. Results show that pervasive up-temperature fluid flow is not required to drive reactions as previously thought.

Pb isotopic results from all possible source rocks in the Irish Midlands demonstrate that, contrary to popularly help opinions, the Pb in these world class ore bodies was largely derived from the underlying basement rocks and delivered to the ore deposition site by fluid flow in basement fractures. Light stable isotopic studies of the Dalradian Complex indicate large local fluid fluxes and mass transport were important processes throughout the complex.

In addition to the experimental, theoretical, and field studies mentioned above, contributions were made to a variety of other fields. Inverse models were developed to extract information about temperature-pressure-time paths from geospeedometry. Fundamental questions of the Earth's oxygen composition have been addressed. Wavelet analysis has been used to extract details of the time-varying amplitudes of harmonics contributing to the ice-age cycles. Global weathering cycles have been summarized and explained theoretically. Multi-species flow and transport modeling has extended our views of water-rock interaction. Isotopic and *ab initio* methods have unraveled fundamental puzzles in the chemistry of Earth's atmosphere.

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