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DOE Workshop: Sedimentary Systems, Aqueous and Organic Geochemistry

Lawrence Berkeley Laboratory

July 15–16, 1993

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DOE Workshop: Sedimentary Systems, Aqueous and Organic Geochemistry, July 15-16,1993, Lawrence Berkeley Laboratory

Agenda

July 15,1993; Bldg. 50 Auditorium, LBL

8:45 A.M. Welcome, Introduction - William Luth

1. Fundamental Properties

9:00 A.M. L.M. Anovitz, University. of Arizona
Electrochemical determination of the Gibbs free energy of rock-forming minerals

9:20 J.G. Blencoe, Oak Ridge National Lab.
Crustal stability of C-O-H N fluids

9:40 R.J. Bodnar, Virginia Polytechnical Institute & State University.
PVTX properties of fluid systems

10:00 A. Navrotsky, Princeton University.
Thermodynamics of minerals stable near the earth's surface

10:20 K. S. Pitzer, Lawrence Berkeley Lab. and Dept. of Chemistry, University of California, Berkeley
Thermodynamics of high temperature brines

10:40 Break

10:55 P.S.Z. Rogers, Los Alamos National Laboratory.
Thermodynamic properties of aqueous solutions at high temperature and pressure

11:15 R.H. Wood, University of Delaware
Development of an experimental data base and theories for prediction of thermodynamic properties of aqueous electrolytes

11:35 D.G. Miller and J.A. Rard, Lawrence Livermore National Laboratory.
Thermodynamics, kinetics, and transport in aqueous electrolyte solutions

2. Geochemical Transport

11:55 K. W. Jones, Brookhaven National Laboratory and W. B. Lindquist, State University of New York at Stony Brook
3-D imaging of drill core samples using synchrotron computed microtomography

12:15 D.J. Wesolowski and R.E. Mesmer, Oak Ridge National Laboratory
Hydrothermal geochemistry

12:45 Lunch

1:45 H.C. Helgeson, University of California, Berkeley
Chemical interaction of petroleum, oil field waters, and minerals in hydrocarbon reservoirs

2:05 A.C. Lasaga, Yale University
Reactive fluid flow models and applications to diagenesis, mineral deposits and crustal rocks

2:25 P. Ortoleva, University of Indiana
Mechano-chemical self organization and nonlinear dynamics in sedimentary basins

2:45 J. Noorishad and C.-F. Tsang, Lawrence Berkeley Laboratory
Development of a numerical approach to study coupled thermohydromechanical processes in geological systems

3. Rock-Water Interactions

3:05 D.R. Cole, Oak Ridge National Laboratory
Stable isotope systematics of fluid/rock interaction

3:25 W.G. Ernst, Stanford University
Fluid flow, element migration, and petotectonic evolution of the Early Mesozoic Central Klamath island arc"

3:45 R.A. Yund and J.R. Farver, Brown University
Grain boundary transport and related processes in fine-grained aggregates

4:05 T.I. Eglinton, Woods Hole Oceanographic Institution
Incorporation of sulfur into organic matter in sediments

4:30-5:30 Visit to the Advanced Light Source, LBL

July 16

8:30 A.M. D.R. Janecky, Los Alamos National Laboratory
Tracers in geological reservoirs

8:50 J.B. Hulen, University of Utah Research Institute and F.E. Goff, Los Alamos National Laboratory.
Geothermal controls on oil-reservoir evolution in the Basin and Range Province, eastern Nevada

9:10 H. R. Westrich, Sandia National Laboratories, Albuquerque
Mineral hydrolysis kinetics

4. Organic Geochemistry

9:30 R.D. Elmore, University of Oklahoma
Development and application of new methods for constraining time of hydrocarbon migration

9:50 A.K. Burnham, Lawrence Livermore National Laboratory
Compositional kinetic model of petroleum formation

10:20 Break

10:35 L.S. Land,, University of Texas at Austin
The role of mudstones in burial diagenesis

10:55 A.J. Bakel, Argonne National Laboratory
Compound-specific carbon isotopic analysis of petroleums

11:15 C. Barker,University of Tulsa
Stability of natural gas in the deep subsurface

11:35 A. Variavamurthy, Brookhaven National Laboratory
Geochemical incorporation of sulfur into sedimenatry organic matter

11:55 J.K. Wehlan,Woods Hole Oceanographic Institution
Organic geochemistry of continental margin and deep ocean sediments

12:05 C.D. Tait, D.R. Janecky, and J.A. Musgrave, Los Alamos National Lab.
Direct speciation of metal and metalloid ions by optical spectroscopies

12:30 Lunch

5. Sedimentary Systems

1:30 G. Eberli,University of Miami
Sequence stratigraphy, siesmic reflectors and diagenetic changes in carbonates

1:50 G.N. Hanson, State University of New York, Stony Brook
Geochemistry and origin of regional dolomites

2:10 M. Attrep, Los Alamos National Laboratory
Search for evidence of large comet or asteroid impacts at extinction boundaries

2:30 Closing comments, William Luth

Project Summary

Electrochemical Determination of the Gibbs Free Energies of Rock-Forming Minerals

Principal Investigator: Lawrence M. Anovitz
Organization: Department of Geosciences, University of Arizona, Tucson, AZ 85721
Telephone: (602)-621-4618

Scientific and Technical Content

A) Relation to research by others

The derivation of a high quality thermodynamic database for minerals, fluids and aqueous species is a long running and very important effort in a number of geological fields including igneous and metamorphic petrology and aqueous geochemistry. Such data allow us to quantitatively constrain the conditions of fossil systems, to predict the chemistry occurring in inaccessible parts of modern systems (such as hydrothermal fields), and to predict those which might occur in future situations. perhaps for hazard assessment in waste storage questions. Many workers are involved in these fields and depend on the availability of high quality thermodynamic data to make their calculations.

More specifically, the currently ongoing work on the oxide buffers is important to other workers research for at least three reasons. 1) These buffers have commonly been used as redox reference points for other experiments on the stabilities of a wide variety of phases. Unless they are well known, values dependent on them are more uncertain than necessary. 2) The oxide phases themselves occur, more or less commonly, in a variety of important geological and extraterrestrial settings (e.g. porphyry copper deposits, meteorites, nickel deposits) and understanding their stabilities enhances our understanding of the formation of the systems in which they occur. 3) The experiments currently underway are aimed at using the oxide buffer data to better understand the uncertainties in the solid electrolyte method itself. such results will be of importance both in our interpretation of measurements on geologically important phases and in industrial situations where solid electrolytes are used (e.g. steel manufacture, automobile emissions control).

B) Schedule of major research activities

1990 - 1992

1) build laboratory, designed and tested electronics and vacuum systems
2) developed equilibrium method for preparation of reduced iron glass starting materials for synthesis of iron silicates
3) completed preliminary synthesis of ortho- and clinopyroxenes along the enstatite - ferrosilite and diopside hedenbergite joins
4) completed and submitted theoretical reevaluation of mixing properties on the join diopside enstatite, noted potential major uncertainty in our knowledge of the mixing properties of ordered intermediate phases (e.g. diopside)

1992 - present

1) tested techniques and procedures needed to obtain stable results in both one electrolyte and two electrolyte designs
2) measured Gibbs energies of 4 important oxide buffers directly relative to air and in two steps through a gas intermediate stage
3) completed post-review revision of diopside-enstatite paper (revisions underway)
4) testing effects of thermocouple calibration on derived results
5) testing effects of electrical polarization on derived results
6) added humidity monitoring capability to laboratory
7) obtained piston-cylinder apparatus for future synthesis work

8) began synthesis of end-member and subcalcic Co-diopside to investigate properties of ordered intermediate compounds

C) Scientific issues currently being addressed and their significance

see 5A and 5B above, and 6A below

D) Approach and techniques used

- 1 atm gas mixing for synthesis of reduced materials
  - Mo metal crucibles for equilibrium formation of Fe-bearing materials
- piston cylinder apparatus for high pressure synthesis
- solid-electrolyte measurement of the redox state of buffered systems to measure standard state thermodynamic properties and mixing properties of oxidizable or reducible oxides and rock-forming silicates.
  1) single electrolyte experiments vs. an air reference
  2) single electrolyte experiments vs. a solid buffer reference
  3) two electrolyte experiments vs. an air reference through a mixed gas (CO-CO_2) intermediate stage
  4) two electrolyte experiments vs. different gas mixtures to test electrical polarizibility

E) Importance of Solving the problem beding addressed

see 5C

Project Output

A) Summary of progress to date

Two years of funding have been received from the Department of Energy for work in this laboratory. This has yielded the following results. The laboratory itself has been designed, built and tested, and is currently yielding good data. Experiments have been, and are being performed on a number of oxide buffers. These have yielded highly precise results which suggest that there may be larger uncertainties in accepted data for these buffers than is currently appreciated. A method has been devised for "equilibrium" reduction of iron-bearing silicate glasses as starting materials, and synthesis of orthopyroxenes along the join enstatite - ferrosilite is nearly complete. Clinopyroxene glasses on the join diopside - hedenbergite have also been made, but not as yet crystallized. Available experimental data on the join diopside - enstatite have been re-examined and modeled in light of the observation that current solution models suggest that diopside, and by extension other ordered intermediate compounds are metastable with respect to, in this case, a subcalcic diopside and wollastonite, and cobalt-diopside, a phase with a great deal of potential for experimental investigation of this problem has been synthesized.

Three furnaces, complete with necessary support facilities (such as an isolated chilled water line, gas removal line, support framework, gas control lines, vacuum lines etc.) and high precision, "in-house" built electronics have been completed. This includes a Deltec-based gas mixing furnace for synthesis with full computer control of temperature, including "ramp and soak" temperature cycling and as well as of the gas mixture using mass flow controllers. This is a large volume furnace, with a 2.5" diameter, 48" long mullite tube. This was done to provide a 5" long $\pm$ 5°C hot spot. This required revision of the standard design for the

water-cooled brass heads which seal each end of the tube. The standard design, which utilizes two O-rings set into the inner wall of the cooling head will not work, because the precision available in ceramic tubes of this diameter is typically ± 0.1" or poorer. Thus a compression-based design, utilizing larger O-rings was developed which works quite well (Figure 1).

Two furnaces for electrochemical studies are also fully on-line and computer controlled. The first is a two-vacuum chamber, single electrolyte design, and the second utilized a single vacuum chamber, two electrolytes, and a mixed gas chamber whose flow is also under computer control. All necessary environmental and experimental parameters are monitored and logged on a frequency set by the user (we usually log every 15 minutes).

The first reactions being run in the laboratory are the oxide buffer reactions:

$$Ni + 1/2\ O_2 = NiO \quad (1)$$

$$2\ Cu + 1/2\ O_2 = Cu_2O \quad (2)$$

$$Cu_2O + 1/2\ O_2 = 2\ CuO \quad (3)$$

$$0.947\ Fe + 1/2\ O_2 = Fe_{0.947}O \text{ (approximate composition)} \quad (4)$$

Originally these were planned as test reactions, to be compared with the results of O'Neill (1987b, 1988) to calibrate the laboratory. Work to date, however, has yielded very precise results which differ somewhat from those of O'Neill. As these are important reference buffers, both for future experiments in this laboratory and in the literature, a careful set of experiments have been initiated to test their calibration. These are currently underway. Each reaction is being studied relative to air across a single electrolyte, relative to air in two steps with a CO_2/CO gas intermediate, and relative to the other solid buffers. Results to data have been both interesting and encouraging. Very precise results have been obtained from the single electrolyte experiments. Figure 2 shows a single temperature (near 1020 K) for the copper/cuprite reaction. At a given temperature within this array (± 0.1°C precision) the chemical potential of oxygen was obtained with a precision of ± 25 J. Figure 3 shows all of the data for this reaction. Several hundred data points are shown on this figure, the precision of which is much smaller than the size of the points plotted. This type of experiment has been completed for both the Ni/bunsenite and Cu/cuprite reactions, yielding:

$$\mu O_2\ (Ni/NiO) = -472639 + 190.075\ T - 2.10227\ T \ln T\ (\pm 50\ J, T\ K) \quad (5)$$

$$\mu O_2\ (Cu/Cu_2O) = -352011 + 261.578\ T - 14.3584\ T \ln T\ (\pm 20\ J, T\ K) \quad (6)$$

and similar experiments are underway for cuprite/tennorite and iron/wüstite.

Two-electrolyte experiments have been completed for Ni/bunsenite, cuprite/tennorite, iron/ wüstite, and copper/cuprite. The first of these, Ni/bunsenite, yielded stable results which were slightly more reducing than those obtained in the single electrolyte experiments. These results were, however, significantly less precise, with a typical uncertainty of ± 300 J at a given temperature. During the cuprite/tennorite experiments it was discovered that this could be improved by maintaining a better seal and slowing the CO_2 flow rate, and single temperature precisions of ± 130 J were obtained. These are still less precise than the single electrolyte experiments, and we therefore decided to improve these results. Improvements in the electronics reduced the variability for the iron - wüstite buffer to as little as ± 36 J close to that obtained for

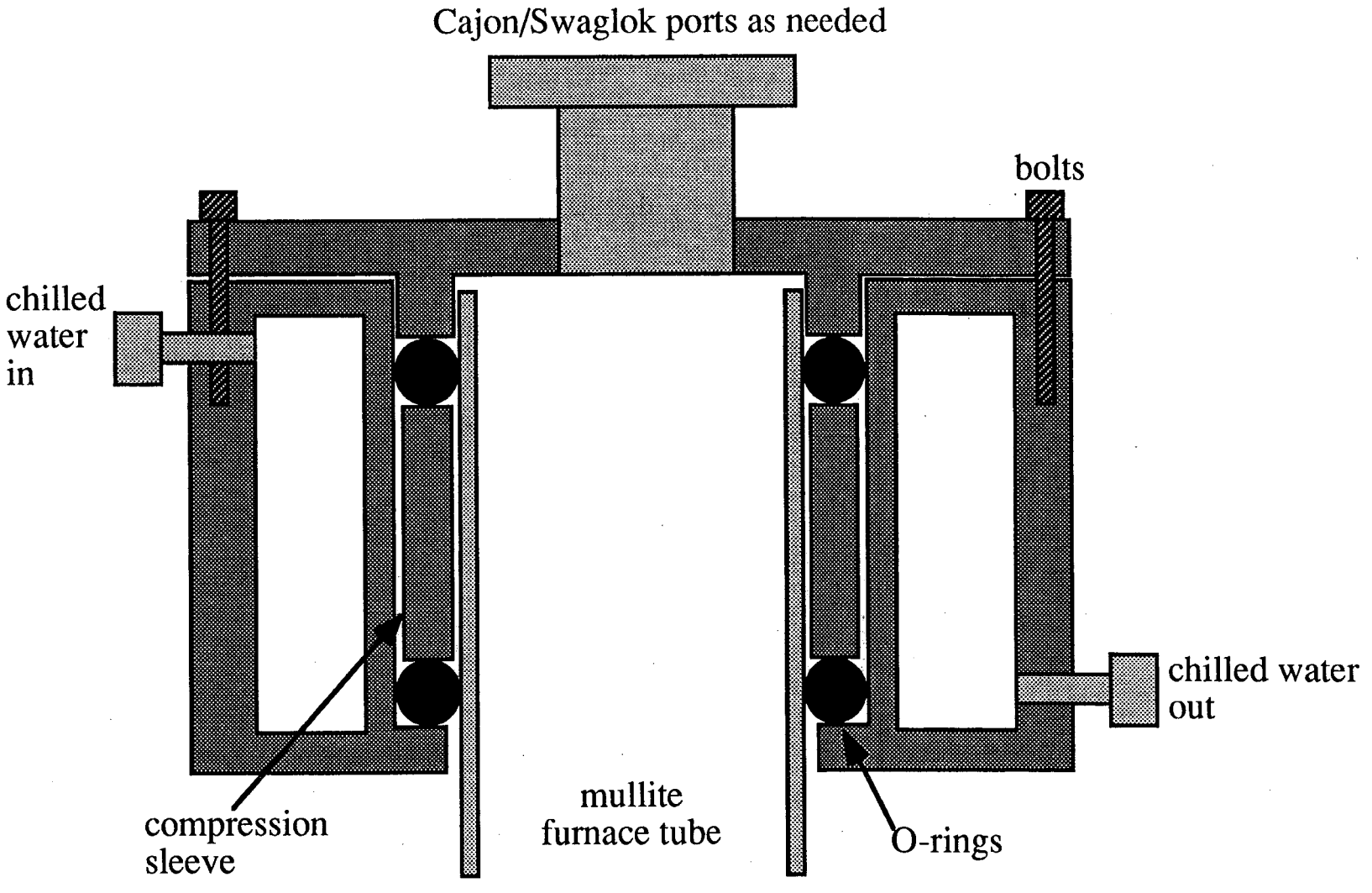

Figure 1: Water cooled sealed head for large diameter gas-mixing furnaces (Schematic). Large diameter ceramic tubes are often significantly out of round and need more flexible sealing systems. In this design the flange on the bottom of the top plate compresses 2 large O-rings - the upper directly, and the lower through the compression sleeve. The large diameter of the O-rings and this direct compression allows them to distort sufficiently under compression to correct for significantly out-of round furnace tubes.

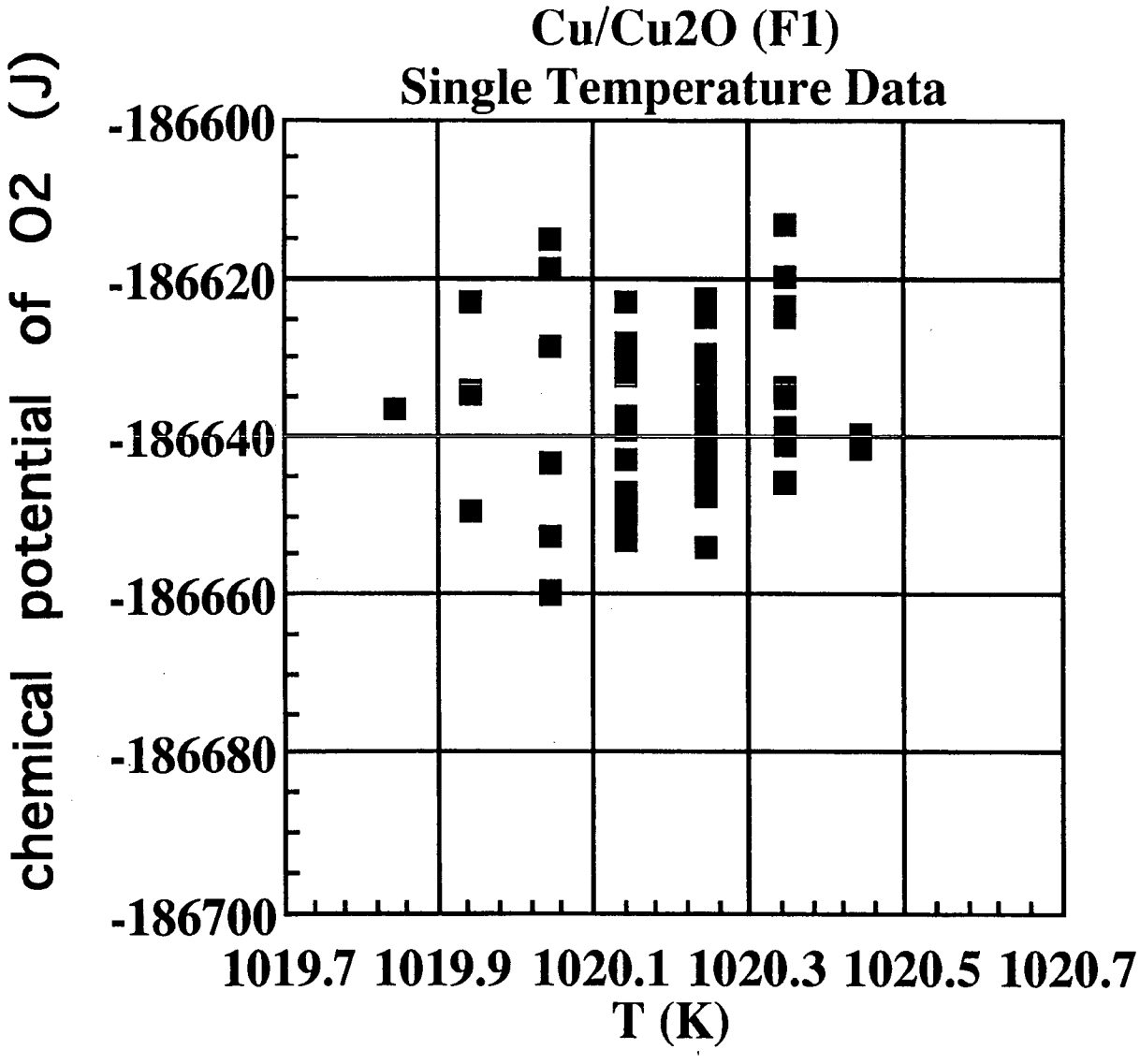

Figure 2: Measured values for the copper - cuprite reaction at a single temperature setpoint near 1020 K. At any given temperature within this array the scatter of the data is less than ± 25 J.

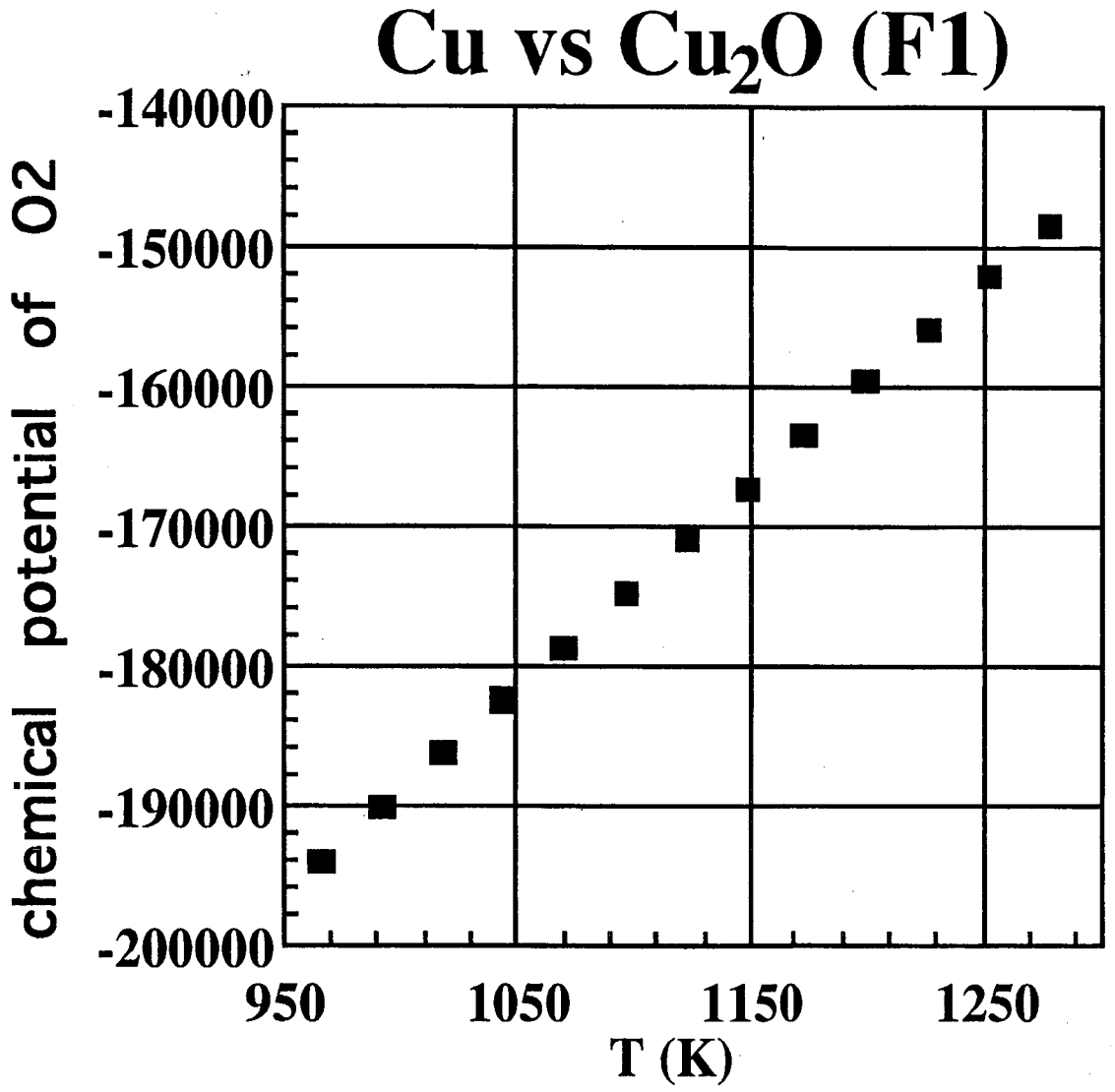

Figure 3: Data for the copper - cuprite reaction obtained in furnace 1. Each of the points shown in actually a large number of measurements, the combined scatter of which is much smaller than the symbol size.

the single electrolyte furnace, and re-runs of the Ni/bunsinite and cuprite/tennorite buffers improved those results. Results for all 4 buffers from this furnace are:

$$\mu O_2 (Cu_2O\text{-}CuO) = - 284341 + 321.545\ T - 16.5191\ T \ln T\ (\pm\ 128\ J, T\ K) \quad (7)$$

$$\mu O_2 (Cu\text{-}Cu_2O) = - 389722 + 561.037\ T - 52.4281\ T \ln T\ (\pm\ 98\ J, T\ K) \quad (8)$$

$$\mu O_2 (Fe\text{-}"FeO") = - 504845 - 65.2270\ T - 24.9260\ T \ln T\ (\pm\ 36\ J, T\ K) \quad (9)$$

$$\mu O_2 (Ni\text{-}NiO) = - 504238 + 425.409\ T - 31.7910\ T \ln T\ (\pm\ 60\ J, T\ K) \quad (10)$$

Both the Ni/bunsenite and cuprite/tennorite results are more reducing than results in the single electrolyte experiment, and all six sets of experiments yield slightly different results from those reported by O'Neill (1987b, 1988). The two-electrolyte experiments reduce the voltage across any single electrolyte, and thus the potential effects of non-Nernstian behavior and electrical polarization. The uncertainties are small enough, however, that temperature errors of 10°C or less are sufficient to explain all of the differences between the results. In typical reversal experiments such temperature uncertainties are generally ignored, as being smaller than other sources of error in the experiment. The high potential precision of the electrochemical approach, however, suggests that greater accuracy in temperature measurement is warranted. Thermocouples will therefore be calibrated using a primary standard thermocouple obtained from AESAR whose calibration is directly traceable to NIST standards. The thermocouple calibration apparatus has just been completed, and we now plan to calibrate the thermocouples which were set aside after each experiment. These will then be calibrated and the experimental temperatures and fitting equations revised accordingly. We are also completing experiments in the 2-electrolyte furnace in which the gas mixture proportions are varied in order to change the voltage across the sample electrolyte. As there should be no polarization when the voltage across this cell is zero, we should be able to directly calibrate the effects of this problem for each of the buffers in this manner.

Experiments on the binary pyroxene joins first require that the appropriate materials be synthesized. A great deal of work has been completed on the synthesis of orthopyroxenes for these study, although all of the available sample require at least one more piston cylinder run to more fully homogenize their compositions.

The first step in this synthesis was to obtain suitable starting materials. These can be either oxide mixtures or glasses. Oxide mixtures have the disadvantages of being less homogeneous, and of not containing iron in the correct oxidation state, as stoichiometric FeO does not exist. Most syntheses of iron-bearing silicates thus are done using glasses made by melting and reducing the initial oxide mixtures. These glasses have the further advantage of being very reactive. They are usually made (cf. Bohlen and Boettcher, 1981) by melting the oxides in capped graphite crucibles. This approach, however, has two disadvantages. First, it is inherently a disequilibrium experiment. Because the oxygen fugacity of graphite is within the stability field of iron metal, experiments which are run too long, or at too high a temperature, yield metallic iron "balls" in a silicate glass, rather than a homogenous iron-silicate glass. Secondly, because most of the reduction occurs when the material is in the liquid phase, oxygen exchange becomes difficult, as the oxygen must diffuse through the melt to equilibrate with the surrounding reduced atmosphere.

It would be advantageous, therefore, to devise a technique in which divalent iron is stable at temperature, so that the experiment is time independent and can be run as long as needed to assure complete reduction to Fe^{2+} without formation of iron metal, and in which the reduction can be done while the material is still a powder. Such a technique was devised during these experiments. The first step was to choose a crucible material. Molybdenum metal is stable at oxygen fugacities slightly above those at which iron oxidizes to wüstite, and there is little solid solution between Mo metal and Fe oxide. The gas mixing furnace can therefore be used to put a molybdenum crucible containing an iron-silicate oxide powder mixture under conditions where the molybdenum will remain a metal and ferric iron will reduce to ferrous iron but not iron metal. After a suitable time for reduction (6 - 12 hours) the temperature can then be raised above the melting point and then cooled to form a glass (± quench crystals).

The first difficulty with this technique was obtaining the Mo crucibles. Mo metal is very hard, and local machinists were not equipped to work it. We therefore fabricated a press in which Mo sheet (0.005") can be pressed into small crucibles that look like high-sided bottle caps. If the sides are made too high, the bottom may split out of the crucible, but otherwise good results are obtained. Having fabricated the crucibles, we devised the rest of the procedure while at the same time testing the gas mixing furnace, and completed glasses for all of the orthopyroxene and clinopyroxene compositions described below. In some cases quench crystals were formed, but all "glasses" were thoroughly crushed and ground in an agate mortar and a SPEX mill to assure homogeneity.

Having completed the starting materials, the next step was to crystallize the orthopyroxenes. This proved more difficult to arrange than expected. We had originally proposed to carry on this stage of the work in the laboratory of Dr. Ganguly here at the University of Arizona. Unfortunately, his laboratory become so busy that he was unable to give us any experimental time. Arrangements were then made for the student working on this project, Mr. Samir Bhattacharyya, to spend a month in the laboratory of Dr. Steve Bohlen, USGS Menlo Park, to do this work. In this relatively short time all of the orthopyroxenes were crystallized. Examination with the electron microprobe on Mr. Bhattacharyya's return suggested that a few percent inhomogenaity remains in the samples. A final run at higher temperatures will therefore improve the quality of the synthetic materials.

This experience showed that future work in this laboratory cannot rely on access to other laboratories for the synthesis of starting materials. Funds from another source have therefore been used to purchase a piston cylinder apparatus. This will be shared with Dr. Mark Barton of this department, who is also building a series of small internally-heated gas apparatuses for the shared facility. Thus we will both have access to needed high pressure experimental facilities. The PC was ordered from Mr. Peter McNutt of Rockland Research. It has now arrived, as have all of it's electronic and other components, and is being set up, and we expect it to be operational this summer.

As a preliminary to the reevaluation of quadrilateral pyroxene activity/composition data which will be done on completion of the binary electrochemical experiments, I undertook an examination of a/X relationships on the diopside - enstatite join. Examination of available models shows that all predict that end-member diopside is metastable with respect to wollastonite and a sub-calcic diopside as a necessary

condition of the Margules model applied to the $CaMgSi_2O_6$ - $Mg_2Si_2O_6$ portion of the $Mg_2Si_2O_6$ - $Ca_2Si_2O_6$ join (Figure 4). Available experimental data suggest that this is unreasonable, as at high temperatures the variation from end-member of a diopside synthesized or otherwise formed "on-composition" should be significant. A reevaluation of phase equilibria along this join was therefore undertaken involving both examination of the stabilities of the various $Mg_2Si_2O_6$ polymorphs and reformulation of the solvus model.

Evaluation of the stabilities of the $Mg_2Si_2O_6$ polymorphs shows that a great deal of uncertainty remains. Discrepant experimental data on the low-clinoenstatite ($P2_1/c$) to orthoenstatite (Pbca) transition cannot be reconciled by any possible reaction curvature, and a preferred data set cannot be chosen. Similarly, several sets of experimental data suggest stability fields for C2/c clinoenstatite, but two such fields may exist, one at high and one at low pressures. The relationship between these two fields remains uncertain. The orthoenstatite - protoenstatite (Pbcn) transition is somewhat better known. If only half-reversals are considered the experiments are consistent with a transition located between:

$$T\ (°C) = 975 + 0.0500\ P\ (bars) \quad (13)$$

$$T\ (°C) = 995 + 0.0425\ P\ (bars) \quad (14)$$

However, extrapolation of available thermodynamic data suggest that this reaction may not be linear, but may curve to lower pressures at higher temperatures (Figure 5).

In order to use the Margules formulation to model the solvus while retaining end-member diopside as a stable phase it is necessary to consider the join $Mg_2Si_2O_6$ - $Ca_2Si_2O_6$. Such a model reproduces the available experiments as well as currently available models below 50 kb and 1773 K, but is mathematically inflexible and yields coefficients which can at best be considered fitting parameters. In addition, the qualitative shape of the $\Delta G/X$ curve for diopside, and therefore the activity/composition relations suggested by this model is unusual. The equations for diopside do not reduce to $a = X$ for all compositions as W is reduced to 0. As the model accurately reproduces the solvus data, this analysis suggests that calculated activities for ordered intermediate compounds such as diopside are very model dependent. Direct measurement of the activities of such compounds are needed in order to ascertain the appropriate shape of the $\Delta G/X$ curves for such materials. As the model presented in this paper both reproduces the solvus and does not predict that end-member diopside is metastable, however, it is regarded as an improvement over other models currently available in the literature. This paper is currently undergoing post-submission revisions which have eliminated a number of problems encountered in the earlier formulations.

The most significant result of this work is the realization that activities derived from mathematical formulations which fit solvus data may or may not yield real activity/composition relations for compositions outside the solvus, even if the solvus is well fit. This appears to be especially true for ordered-intermediate phases such as diopside. One part of the research currently underway is aimed directly at obtaining such data for at least one such phase, in this case $CaCoSi_2O_6$ (cobalt diopside). Because the a/X relations predicted by the newer formulation are qualitatively different from those in older work, such an experiment should be able to compare the two approaches. We are currently synthesizing both end-member Co-diopside and various subcalcic compositions whose Gibbs free energies will be measured in order to test the a/X relations predicted by the theoretical work just described.

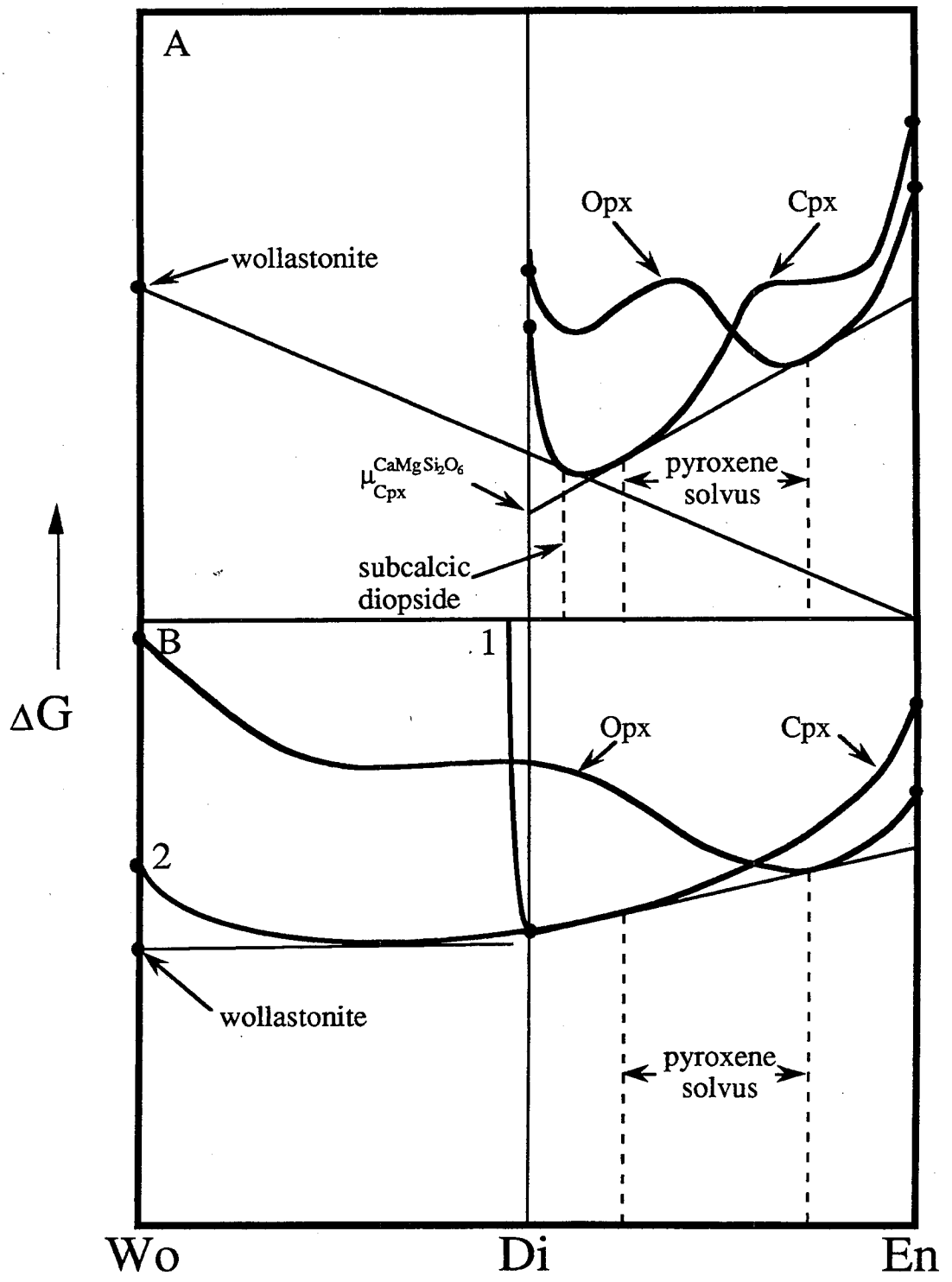

Figure 4: Theoretical DG/X curves for the wollastonite - diopside - enstatite join.

A: Model treating clino- and orthopyroxenes as separate solutions on the diopside - enstatite subjoin. Dots show the Gibbs energies of stable and fictive end-member phases, light lines connect stable mineral pairs. The chemical potential of diopside in a clinopyroxene on the solvus is significantly different from end-member diopside. Diopside is metastable with respect to a subcalcic diopside and wollastonite.

B: Model treating the entire wollastonite - enstatite join in which diopside remains stable. Two methods of treating the wollastonite - diopside half of the join are shown. Curve 1 approximates reality. The curve bends steeply away from diopside, and little excess Ca is predicted. Curve 2 predicts fictitive phase equilibria for this half of the join, but is easier to fit with standard models. As only half of the curve is used to fit real data this model is less flexible for a given number of parameters than that shown in part A.

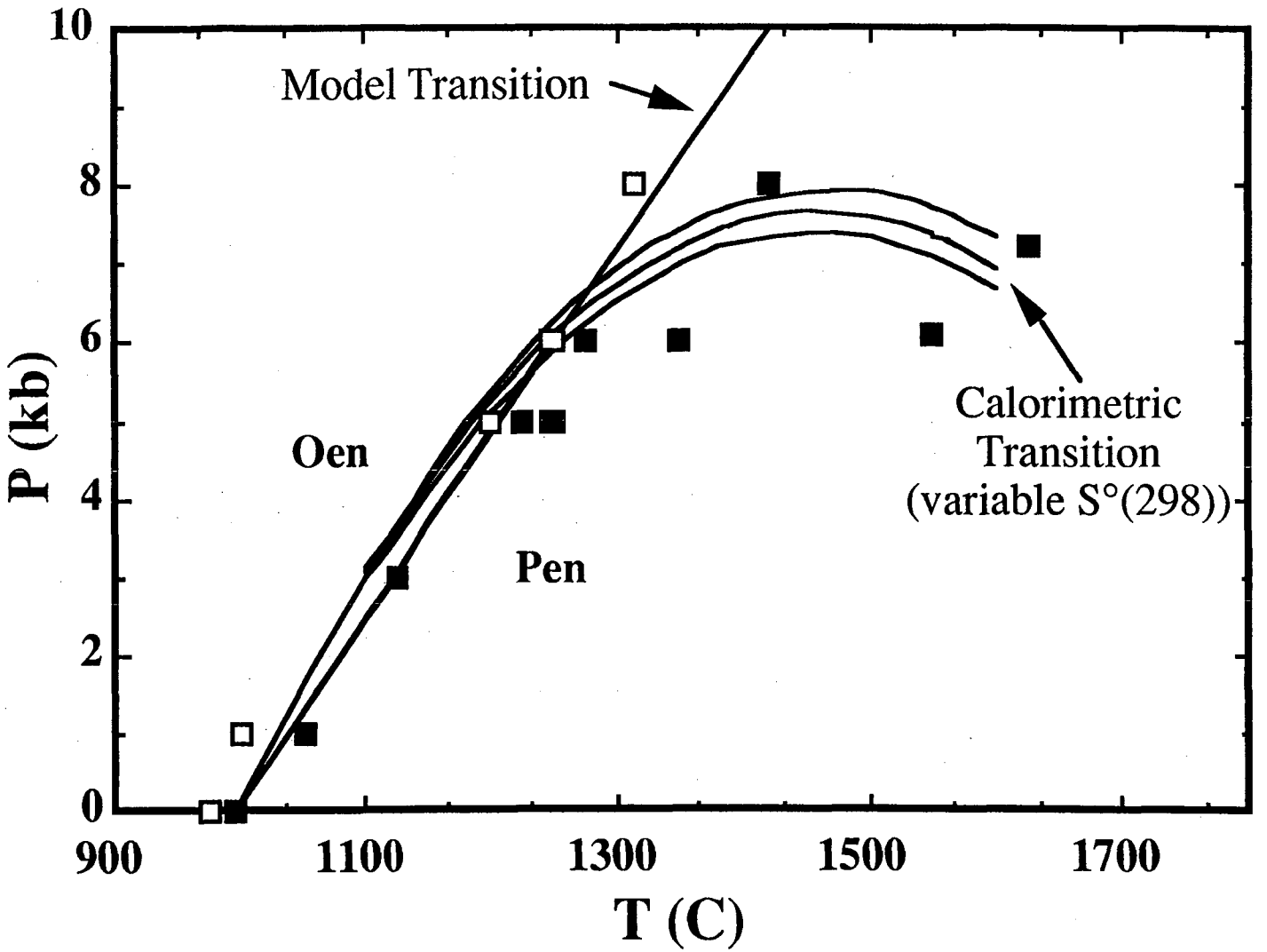

Figure 5: Experimental data constraining the orthoenstatite - protoenstatite transition (Atlas, 1952, Boyd et al., 1964; Kushiro et al., 1968; Anastasiou and Seifert, 1972; Chen and Presnall, 1975) The straight line predicted by the model fits all of the available half reversals. The curved lines are calculated from available thermodynamic data (Table 2), with different estimates of S°(298) from 165.7 J/mol•K to 165.8 J/mol•K for protoenstatite. This also fits most of the experimental data, but predicts a maximum pressure of 7 to 8 kb for the stability of protoenstatite. It is uncertain whether this effect is real or due to extrapolation of the thermodynamic data.

B) Bibliography of papers supported in whole or in part by this grant

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Anovitz, L.M. (1991) Al - zoning in pyroxene and plagioclase: window on late prograde/early retrograde P-T paths in granulite terranes. *Amer. Mineral.*, 91, 1328 - 1343.

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Bhattacharyya, S. K. (1993) Measurement of the Gibbs Free Energy of some metal oxide reactions. University of Arizona Geosciences Symposium, April 7, 1993.

Bhattacharyya, S. K. and Anovitz, L.M. (1993) Measurement of the Gibbs Free Energy of some metal oxide reactions. Abst. in prep. To be submitted for Fall, 1993, GSA meeting.

Bhattacharyya, S. K. and Anovitz, L.M. (1993) Measurement of the Gibbs Free Energy of some metal oxide reactions. Paper in prep. To be submitted to American Mineralogist.

MEASUREMENT OF THE GIBBS FREE ENERGY OF SOME METAL-OXIDE REACTIONS

Bhattacharyya, S.K. and Anovitz, L.M. Department of Geosciences, University of Arizona, Tucson, AZ 85721

An electrochemical approach has been used to measure the chemical potential of oxygen (μO_2) buffered by a number of metal-oxide reactions. The experiment utilizes solid electrolytes to measure μO_2 of a reaction by monitoring the voltage generated between the metal-metal oxide assemblage and an oxygen reference such as air, a known solid buffer, or a buffered gas mixture. High temperature electrochemical cells using calcia-stabilized zirconia as an oxygen specific electrolyte with air and air/carbon-dioxide as reference electrodes, have been used for these experiments. Two types of experiments, utilizing single electrolyte and two electrolyte methods, have been performed. This allows greater experimental flexibility and cross checking of results for internal consistency. Each reaction has been studied relative to air across a single electrolyte in the one-cell furnace, and relative to air with a carbon-dioxide gas intermediate step in the two-cell furnace. Very precise results have been obtained from the single electrolyte experiments (± 20 J at any T). The two-electrolyte method was initially less precise (± 250 J at a given T for the first Ni-NiO run) but this deviation was reduced to as little as ± 36 J in later runs. These experiments yielded,

from the single electrolyte design:

for Ni-NiO : μO_2 = -472639 + 190.075 T - 2.10227 T ln T (± 50 J, T in Kelvin)

for Cu-Cu_2O : μO_2 = -354024 + 271.081 T - 15.4506 T ln T (± 47 J, T in Kelvin)

and from the two electrolyte design:

for Ni-NiO : μO_2 = - 504238 + 425.409 T - 31.7910 T ln T (± 60 J, T K)

for Cu-Cu2O : μO_2 = - 389722 + 561.037 T - 52.4281 T ln T (± 98 J, T K)

for CuO-Cu_2O : μO_2 = - 284341 + 321.545 T - 16.5191 T ln T (± 128 J, T K)

for Fe-"FeO" : μO_2 = - 504845 - 65.2270 T - 24.9260 T ln T (± 36 J, T K)

The small differences between the two types of experiments may be due to temperature uncertainties and/or electrical polarization. Experiments are underway to evaluate these possibilities. Results from the present study are in reasonable agreement with those of O'Neill (1987,1988), although small systematic differences exist. These may reflect temperature uncertainties as differences of ± 5°C are sufficient to explain the observed variations.

The data obtained in this study have both direct geological applications and importance in the derivation of the thermochemical properties of other rock-forming minerals. Ni is a compatible element which readily substitutes into the olivine structure. It is also siderophile and may partition into a metallic phase during core formation, as will metallic iron. Copper, cuprite and tenorite occur in a wide range of copper deposits. All three systems are also of metallurgical interest. In addition, these reactions have been widely used as reference buffers for experiments on a number of iron-bearing phases. The thermodynamics of these metal-oxide systems are thus essential to precise quantification of these other systems.

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Crustal Stability of C-O-H-N Fluids

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Overview

Experimental studies are being performed to delineate the thermodynamic mixing properties of C-O-H-N fluids and the decomposition kinetics of acetic acid and sodium acetate at elevated pressures and temperatures. The ultimate goal of the research is to develop comprehensive equations of state for C-O-H-N fluids, and to model the role of carboxylic acids in the migration of natural gas in sedimentary basins.

Introduction

Throughout the lithosphere, fluids composed predominantly of carbon, oxygen, hydrogen and nitrogen have played a key role in transporting and localizing a wide variety of energy and mineral resources. Thus, it is unfortunate that so little is known about the thermodynamic mixing properties of these fluids at mid- and upper-crustal P-T conditions (1-4000 bars, 50-700°C). The best way to mitigate this problem is to acquire experimental data that can be used to develop accurate thermodynamic models for C-O-H-N fluids.

Acetic acid is the most abundant short-chain aliphatic acid in hydrothermal sedimentary environments (Bell et al., 1993, and references therein). It occurs in petroleum brines at concentrations up to 0.17 mol/kg. More importantly, there is evidence that acetic acid/acetate plays a major role in several important basinal processes. For example, it has been suggested that acetic acid influences the development of "secondary porosity" in sediments associated with petroleum deposits. Secondary porosity forms as a result of dissolution of alkali feldspar, plagioclase and calcite grains, and it is a key factor in the migration and accumulation of petroleum and natural gas. Acetate can potentially influence the formation of secondary porosity by complexing aluminum (thereby accelerating the dissolution of feldspars), and by buffering the pH of basinal brines (thereby affecting the dissolution and precipitation of carbonate). Geochemists have also theorized that: (1) acetate acts as a reaction intermediate in the primary migration of natural gas (Kharaka et al., 1983), (2) acetate is involved in homogeneous redox processes with other metastable carboxylates (Shock, 1988), and (3) acetic acid/acetate plays an important role in the transport of ore metals to sites of deposition in sediment-hosted ore deposits (Drummond and Palmer, 1986). Clearly, there is ample scientific justification for research that provides new information on the stability of acetate in sedimentary-basin systems.

Objectives and Approach

Available experimental data are insufficient to permit accurate quantitative modeling of the thermodynamics and kinetics of C-O-H-N fluids at elevated pressures and temperatures. To address this problem, project personnel are actively engaged in experimentation that is designed to elucidate the thermochemical properties and reaction kinetics of these fluids. To date, emphasis has been given to three research activities: collecting P-V-T data on C-O-H-N

gases, measuring the activity-composition relations of aqueous C-O-H-N fluids, and performing rocking autoclave experiments which provide data on the stability of acetic acid and sodium acetate. These research "tasks" are summarized in the paragraphs below.

P-V-T Properties of C-O-H-N Fluids

Experimental Methods—*P-V-T* data for pure C-O-H gases (CO_2 and CH_4) and binary and ternary CO_2-CH_4-N_2 gas mixtures are being collected using a unique vibrating-tube densimeter (VTD) that is designed to measure the volumetric properties of fluids at *P-T* conditions as high as 3500 bars and 500°C (Blencoe, 1990; Seitz et al.,1992; Seitz et al., manuscript accepted for publication). In these experiments, an isobaric, isothermal flow-through method is employed to obtain a statistically significant number of measurements (n = 100-400) for the period of vibration at each *P-T-X* condition. High-accuracy (±0.05%) positive-displacement pumps are used to deliver the gases to the vibrating tube. Gas mixtures are formed by flowing pure gases (CO_2, CH_4, and N_2) into T-junctions on the upstream side of the vibrating tube. Pressure and temperature are controlled to ±0.1 bar and ±0.01°C, respectively. Conservative estimates of accuracy are: *P*, ±2.0 bar; and *T*, ±0.2°C. Precisions of experimentally determined molar volumes typically range from 0.05 to 0.5%, and vary as a function of the density and composition of the gas mixture.

Data Reduction and Thermodynamic Analysis—Densities of "unknown" C-O-H-N gases are derived from VTD readings (Fig. 1) using equations of the form

$$\rho = a + b\tau^2, \qquad (1)$$

where ρ is the density of an "unknown" gas, τ is the densimeter reading (measured period of vibration) for the unknown gas, and *a* and *b* are regression coefficients that depend on the physical and mechanical properties of the vibrating tube. These linear "calibration" equations are derived from ρ and τ^2 data for three standards (He, N_2 and Ar). The density of an unknown gas is calculated by substituting the τ^2 value for that gas into eq. (1).

Density data for pure C-O-H gases (CO_2 and CH_4) are used to calculate molar volumes for these gases. Density data on binary and ternary CO_2-CH_4-N_2 fluids are used to calculate molar volumes and excess molar volumes for these mixtures. The excess molar volume (V^{ex}) of a gas mixture can be calculated from its molar volume and the molar volumes of the end-member gases using the identity

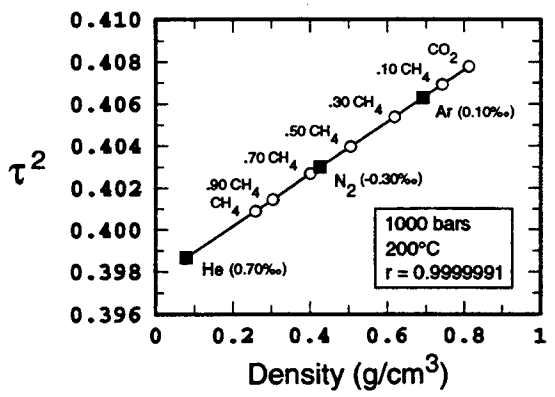

Fig. 1. The relationship between density and the square of the vibrational period for standard gases (filled squares) and a series of CO_2-CH_4 gas mixtures (open circles). The line represents a linear least-squares fit to the data for the standard gases. Values in parentheses indicate the extent to which data for standard gases deviate from the regression line, in parts per thousand.

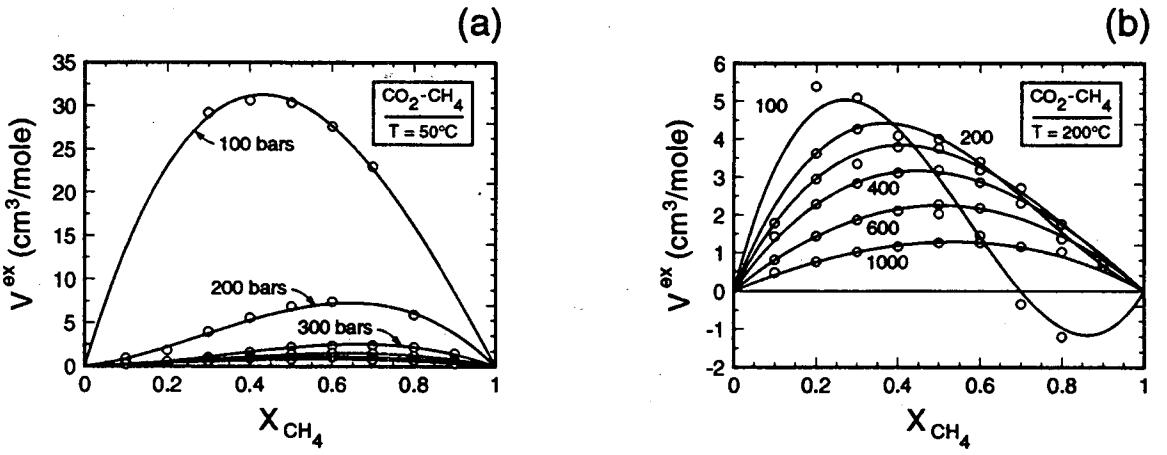

Fig. 2. *P-V-T* data for CO_2-CH_4 mixtures at (a) 50°C, and (b) 200°C.

$$V^{ex} = V - \sum_{i=1}^{n} X_i V_i, \tag{2}$$

where X_i is the mole fraction of gas species i in the mixture, and V_i is the molar volume of pure gas species i. Values for V^{ex} obtained from eq. (2) can be used to develop equations of state which yield calculated fugacities for the individual gas species in binary and ternary CO_2-CH_4-N_2 mixtures.

Results to Date—We have acquired a large quantity of data on the molar volumes of pure CO_2, pure CH_4, and binary and ternary CO_2-CH_4-N_2 mixtures, at 100-1000 bars, 50, 100, and 200°C. Our principal experimental results for the mixtures are outlined below.

1. We have observed both positive and negative excess volumes in CO_2-bearing binary and ternary mixtures (e.g., Figs. 2 and 3).
2. Most of our V^{ex} data for binary mixtures are accurately represented by two-parameter Margules equations.
3. V^{ex} for binary and ternary CO_2-bearing mixtures increases sharply near the critical point of CO_2 (31.1°C, 73.6 bars). For example, see the V^{ex} curve for 50°C, 100 bars in Fig. 2(a).

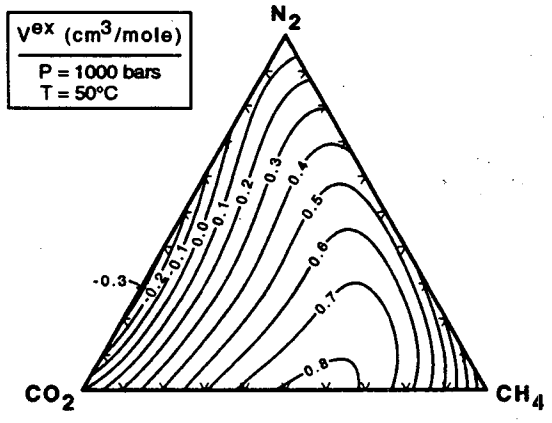

Fig. 3. Experimentally determined excess molar volumes for ternary CO_2-CH_4-N_2 mixtures at 1000 bars, 50°C.

4. For all binary and ternary CO_2-CH_4-N_2 mixtures, V^{ex} increases sharply from zero at very low density (P near 0) to a maximum value at a pressure between 100 and 300 bars. Above this maximum, V^{ex} decreases rapidly with increasing pressure.
5. Between 50 and 200°C, the effect of temperature on V^{ex} is small (except near the critical point of CO_2, as mentioned above).
6. The volumetric properties of ternary CO_2-CH_4-N_2 mixtures (e.g., Fig. 3) can be estimated with good accuracy from V^{ex} data for the binary mixtures, using several different types of geometric projection techniques (Seitz et al., 1992).

Activity-Composition Relations of C-O-H-N Fluids

Experimental Methods—Experiments designed to determine the activity-composition relations of C-O-H-N fluids are performed in a hydrogen-service, internally heated pressure vessel. Control and measurement of hydrogen fugacity (f_{H_2}) is accomplished using a H_2-permeable membrane, which consists of a sealed, internally supported, thin-walled $Ag_{25}Pd_{75}$ tube connected to a gauge and an external hydrogen reservoir. H_2 diffuses through the membrane in response to a gradient in f_{H_2}. During experimentation, f_{H_2} in Ag-Pd encapsulated samples is essentially equal to P_{H_2} in the membrane.

Activity-composition relations for H_2O-CO_2 gas mixtures are being determined using a controlled-f_{H_2O} technique (Joyce and Holloway, 1993) that is based on the equilibrium $H_2 + 1/2O_2 = H_2O$. The equilibrium constant for this reaction,

$$K_w = \frac{f_{H_2O}}{f_{H_2}(f_{O_2})^{1/2}}, \tag{3}$$

yields the identity

$$f_{H_2O} = K_w f_{H_2}(f_{O_2})^{1/2}, \tag{4}$$

which shows that, at a given P and T, f_{H_2O} is proportional to f_{H_2} and $(f_{O_2})^{1/2}$. Thus, buffered values of f_{H_2O} are produced by independently fixing f_{H_2} and f_{O_2}. In each experiment, f_{H_2} is controlled and measured with the H_2-permeable membrane described above, and f_{O_2} is controlled by an f_{O_2} buffer—either Ni-NiO or Co-CoO. After experimentation, the mole fractions of H_2O and CO_2 are determined using a weight-loss technique.

Data Reduction and Thermodynamic Analysis—From the definitions $\gamma_{H_2O} X_{H_2O} = f_{H_2O}/f^{\circ}_{H_2O}$ and $f^{\circ}_{H_2O} = P_{tot}\Gamma^{\circ}_{H_2O}$ (P_{tot} = total pressure, $\Gamma^{\circ}_{H_2O}$ = the fugacity coefficient for pure H_2O), it is evident that, in an aqueous mixture,

$$\gamma_{H_2O} = \frac{f_{H_2O}}{X_{H_2O}\Gamma^{\circ}_{H_2O}P_{tot}}. \tag{5}$$

Values for f_{H_2O} and $\Gamma^{\circ}_{H_2O}$ are provided by eq. (4) and Burnham et al. (1969), respectively. X_{H_2O} is measured experimentally, as discussed above. Eq. (5) shows that controlled-f_{H_2O} experiments yield values of γ_{H_2O} for single-phase aqueous fluids, regardless of the total number of components in the fluids.

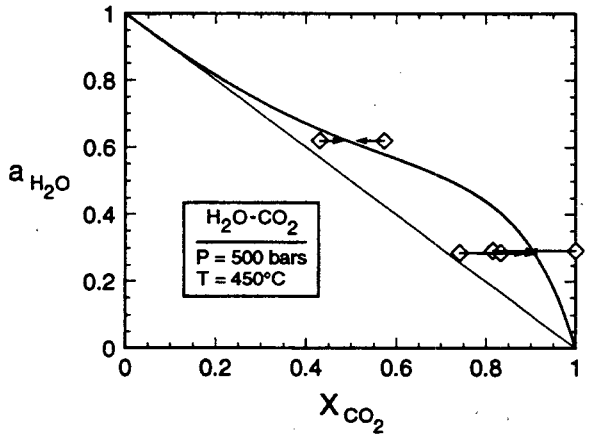

Fig. 4. Experimental data and corresponding activity-composition relations for H_2O-CO_2 fluids at 500 bars, 450°C. Open diamonds represent starting fluid compositions, and arrows illustrate final fluid compositions.

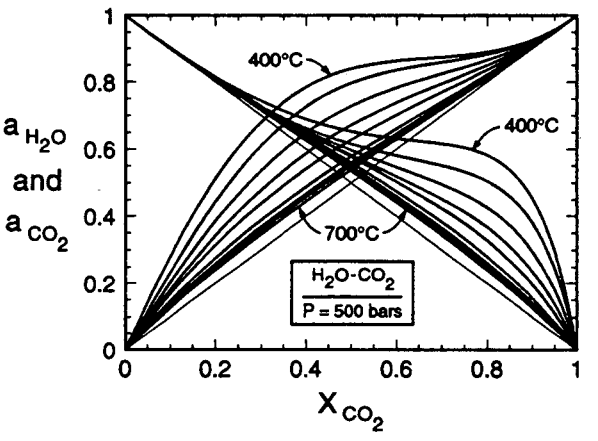

Fig. 5. Experimentally determined activity-composition relations for H_2O-CO_2 fluids at 500 bars, 400–700°C.

Once the compositional dependence of γ_{H_2O} has been determined accurately, activity coefficients for the other fluid components can be calculated by evaluating the mixing parameters of a thermodynamic expression for $ln\,\gamma_{H_2O}$. This equation can be expressed in generalized form as follows:

$$ln\,\gamma_{H_2O} = f(X_{H_2O},\ X_2,\ ...,\ X_n;\ W_{H_2O},\ W_2,\ ...,\ W_i), \tag{6}$$

where X_2, ..., X_n are the mole fractions of non-aqueous components in the fluids, and W_{H_2O}, W_2, ..., W_i are mixing parameters of an empirical thermodynamic formulation.

Results to Date—A series of controlled-f_{H_2O} experiments were performed for H_2O-CO_2 mixtures at 500-1000 bars, 400-700°C. The resulting data have been used to derive bracketed (reversed) values of water activity (a_{H_2O}) for various values of X_{H_2O} at each set of experimental *P-T* conditions (e.g., Fig. 4). To date, 25 reversed values of a_{H_2O} have been determined. Following the thermodynamic procedures outlined above, these a_{H_2O} data have been used to evaluate the mixing parameters of the two-parameter Margules formulation (W_{G,H_2O} and W_{G,CO_2}), which yield calculated *a-X* relations for H_2O-CO_2 mixtures at each set of experimental *P-T* conditions.

Fig. 5 illustrates all of the activity-composition curves for H_2O-CO_2 fluids that we've developed from our experimental data for 500 bars, 400-700°C. It is evident from this figure that, at 500 bars, H_2O-CO_2 fluids become very nonideal at temperatures below ~500°C. At temperatures below ~315°C at 500 bars, a_{H_2O}-X_{CO_2} and a_{CO_2}-X_{CO_2} curves would be sigmoidal in shape, reflecting the presence of two immiscible H_2O-CO_2 fluids.

Stability of Acetic Acid/Acetate

Experimental Methods—Acetate decomposition experiments were performed in "fixed-volume" titanium pressure vessels and a "flexible cell" (gold-bag) apparatus. The primary goal of the experiments was to determine whether the kinetics of acetate decarboxylation are affected significantly by the presence of solids such as natural quartz, fused quartz, Pyrex, calcite, Ca-montmorillonite, iron-bearing montmorillonite, pyrite, hematite, and magnetite. Fluid starting materials were either 1.0 $mol \cdot kg^{-1}$ acetic acid or 1.0 $mol \cdot kg^{-1}$ sodium acetate. Typically, experiments were performed at 335°C and 355°C for each type of fluid ± solid starting composition, in order to determine the effects of temperature, and to permit extrapolation down to geologically relevant temperatures. It was necessary to select temperatures higher than those in sedimentary basins, because decarboxylation rates at temperatures below 300°C are too slow to be measured in laboratory experiments. Surface area and mass of solution were identical in each experiment. Blank runs were performed in the absence of powdered solid materials to determine rates of "background decarboxylation" attributable to the effects of the inner surfaces of reaction vessels.

Fluids were sampled repeatedly during experimentation, and quench pH was measured for each sample. A Dionex 2020i series ion chromatograph was used to analyze for total acetate, and to check for the presence of additional carboxylic acids. X-ray diffractometry and scanning electron microscopy were used to determine whether the solid starting materials reacted during experimentation.

Results to Date—Our experimental data indicate that gold, fused quartz, titanium oxide, quartz, calcite, and pyrite have minimal effects on the rate of acetate decomposition. Stainless steel, Pyrex, magnetite, and hematite were found to accelerate significantly the rate of acetate decomposition. Ca-montmorillonite and iron-bearing montmorillonite had moderate positive effects on the rate.

The projected half-life for acetic acid/acetate decarboxylation in the presence of an unreactive mineral such as quartz is >5 billion years at 100°C. By contrast, the projected half-life for decarboxylation in the presence of magnetite is 400 years at 100°C. In the experiments with hematite and Fe^{3+} defect-bearing magnetite, evidence was obtained for two competing acetic acid decomposition reactions: decarboxylation and an extremely rapid partial oxidation of acetic acid. The latter phenomenon was accompanied by the formation of polycondensates such as mono- and disubstituted benzenes, naphthenes, and other polyaromatic hydrocarbons. Finally, the experimental data indicate that acetic acid/acetate decomposition depends on the pH of the solution, with the highest rates of reaction occurring at a pH where both acetic acid and acetate are present at similar concentrations.

The experimental results described above suggest that, although acetic acid/acetate is stable in the presence of most common sedimentary minerals, in some hydrothermal systems where suitable mineral surfaces are present, decomposition may be rapid, and, in cases where oxidation occurs, decomposition can produce complex hydrocarbons.

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Missing Abstract

R. J. Bodnar
PVTX properties of fluid systems

Thermodynamics of Minerals Stable Near the Earth's Surface

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The goals of the project are to increase both the data base and the fundamental understanding of the thermodynamics of volatile-bearing mineral phases (amphiboles, micas, clays, zeolites, carbonates) important to surficial, sedimentary, and shallow crustal processes.

The complexity, from a crystal chemical, thermodynamic, and petrologic point of view, of sheet and framework silicates, coupled with their typically small grain size and solid solution substitutions, have made low temperature sedimentary and metamorphic phases less amenable to the techniques of quantitative mineral physics than their high grade metamorphic and igneous counterparts. Diagenesis, low grade metamorphism, and chemical processes in the initial stages of subduction are governed by interplay of kinetic and thermodynamic constraints.

Our interest is in the energetics of stable and metastable low temperature minerals. We have adapted high temperature oxide melt solution calorimetry to the study of heats of formation of minerals containing water and carbon dioxide by using drop-solution calorimetry, in which a sample is dropped from room temperature directly into the molten $2PbO{\cdot}B_2O_3$ solvent in the calorimeter at 700 or 800 °C under a flowing gas atmosphere. The oxide constituents dissolve and the H_2O and CO_2 are evolved in a quantitative and reproducible manner. This methodology has been applied to carbonate-silicate equilibria in the system $CaO\text{-}MgO\text{-}SiO_2\text{-}CO_2$ and we are currently studying the $FeCO_3\text{-}MgCO_3\text{-}CaCO_3$ system, with goals of understanding why the ankerite end-member, $FeCa(CO_3)_2$ does not exist and in refining mixing parameters for the $MgCO_3\text{-}FeCO_3$ and $(Mg,Fe)\ Ca(CO_3)_2$ solid solutions.

Work on hydrous phases concentrates on amphiboles, micas, clays, and zeolites. Several related questions are stressed. The extensive solid solutions in these minerals can be thought of as a series of charge-coupled ionic substitutions, for example

$Si_T = Al_T + Na_A$ (edenite substitution)
$Si_T = Al_T + K_A$
$Mg_M + Si_T = Al_T + Al_M$ (tschermakite substitution)

Are the energetics of these substitutions similar over different compositional series within a given structure type, over different structures, and do they show other crystal chemical systematics? For the zeolite group, how do the energetics of different framework topologies compare at given composition, and how do energies of coupled substitutions and hydration depend on framework topology? For solid solution series, how do the energetics of mixing relate to structural variations? Answers to these questions will improve our ability to predict thermodynamic parameters, model phase equilibria, model rock-water interactions, understand surface reactivity, and generally separate kinetic from thermodynamic factors in low temperature geochemistry.

To apply calorimetric methods to phases containing volatiles, the final state of H_2O and CO_2 on dissolution of the crystalline volatile-bearing phase must be determined. Our early work suggested that H_2O interacted exothermically with $2PbO{\cdot}B_2O_3$ melt under a static air atmosphere. However weight change experiments and chemical analysis of the quenched solvent suggested that little H_2O remained dissolved. Because this final state was not as well constrained as we wished, and because the calorimetric runs had small but significant "baseline shifts", we have modified our experiments to be done under a flowing gas atmosphere (1-2 cc/sec Ar, air, or CO_2), which sweeps the evolved gas out of the hot calorimeter, returns the signal to the original baseline, and creates a well defined final state, namely completely evolved H_2O or

CO_2 gas at 1 atm and calorimeter temperature. This is shown by the following thermodynamic cycle:

Reaction	ΔH (kJ/mol) 700 °C	800 °C
(a) $Mg(OH)_2$ (xl, 25 °C) = MgO(dissolved,T)+H_2O(final state,T)	144.1 ± 3.6	156.0 ± 2.8
(b) MgO (dissolved, T) = MgO (xl, 25 °C)	-36.5 ± 1.0	-44.1 ± 0.7
(c) H_2O (gas, T) = H_2O (gas, 25 °C)	-2.50 ± 0.6	-29.2 ± 0.6
(d) MgO (xl, 25 °C) + H_2O(gas, 25 °C) = $Mg(OH)_2$ (xl, 25 °C)	-82.3 ± 0.8	-82.3 ± 0.78
(e) H_2O (gas, T) = H_2O (final state, T)	0.4 ± 3.8	0.5 ± 3.0

Reactions (a) and (b) represent our calorimetric measurements, and (c) and (d) are taken from the literature, and for the cycle $\Delta H(e) = \Delta H(a) + \Delta H(b) + \Delta H(c) + \Delta H(d)$. ΔH (reaction e) indicates that interaction between H_2O and the solvent and is zero within experimental error. For carbonates analogous cycles apply, and the measurement of the enthalpies of carbonate-silicate reactions such as $MgCO_3 + SiO_2 = MgSiO_3 + CO_2$ confirm the soundness of the method.

The common rock-forming carbonate system is $MgCO_3$-$CaCO_3$-$FeCO_3$. Its thermodynamic properties are still surprisingly poorly known. The nature and energetics of disordering in dolomite are incompletely understood because the disordered state is not fully quenchable. As part of our NSF Science and Technology Center in High Pressure Research (CHiPR) we now have a differential scanning calorimeter (DSC) operating in a piston-cylinder apparatus to 20 kb and 1400 °C. This puts us in the P-T range for direct study of dolomite disordering. These studies will be complemented by drop solution calorimetry on nonstoichiometric (Mg/Ca ≠ 1) dolomites, and the data together will form the basis for thermodynamic modeling of the solid solutions.

The thermochemistry of iron-bearing carbonates is imperfectly constrained; we are developing drop solution calorimetric methods and are refining the enthalpy of formation of siderite, $FeCO_3$. We are also addressing the dolomite-ankerite ($MgCa(CO_3)_2$ - $FeCa(CO_3)_2$) join. A dolomite - like phase extends to about Fe/(Fe+Mg) = 0.7 but appears unstable for higher iron contents. Though this has been discussed, there is no clear structural reason for this instability. Determination of the mixing energetics along both joins (ankerite-dolomite and siderite-magnesite) will elucidate this problem and provide fundamental data for carbonate reactions in sedimentary and metamorphic rocks.

The compositional complexity of amphiboles, micas, clays, and zeolites arises from extensive substitutional solid solutions. We are concentrating on the energetics of calcic amphiboles with edenitic and tschermakitic substitutions. Realizing that end members are other hard to come by, either as natural or synthetic samples, our approach is to obtain, characterize, and measure enough samples in which the two substitutions shown occur simultaneously (and other substitutions are minimal) to be able to fit end-member heats of solution and mixing properties.

The similarity between ΔH_{mix} of tremolite-richterite and fluor-tremolite-fluor-edenite amphiboles suggests that the A site controls the mixing energetics of both solid solutions, with A-site positional ordering and interactions with other cations playing an important role. Because the richterite and edenite exchanges are the two most important A-site substitutions that occur in calcic amphiboles, the same factors will influence the stability of all amphiboles with Na in the A site. Therefore, metamorphic calcic amphiboles with small A-site occupancies should be stabilized relative to compositions with zero or high A-site occupancies, and any natural

amphiboles with high A-site occupancies must have crystallized at a high temperature and presumably cooled relatively fast, thereby preventing exsolution.

In the micas studied, the Mg + Si = 2Al substitution is also associated with a positive heat of mixing asymmetric toward the edenite end. This is consistent with destabilization due to layer mismatch, with a solvus in that system, and with limited extent of Al-substitution in natural systems. The X-ray and NMR data are consistent with significant Al, Si short range order and have been used to formulate configurational entropy models.

The energetics of high silica zeolites poses an intriguing question. In comparing quartz and an open framework such as faujasite, the molar volume increases by a factor of two, but this increase reflects the creation of zeolitic pores rather than major changes in the local bonding within the SiO_4 tetrahedra. The enthalpy of the zeolitic silicas relative to quartz is not very destabilizing and about the same as that of silica glass.

The enthalpy does not increase much as the pores become larger and the density lower. This suggests that the silicate framework is not perturbed much energetically by the presence of these cavities, and the transition from pores behaving as an integral part of the crystal structure to behaving as a second phase with only interfacial interactions is already occurring at this size scale. The data further imply that zeolite synthesis, whether in nature or the laboratory or chemical plant, is more a matter of controlling steric (entropic) factors by appropriate templates than of stabilizing specific framework topologies energetically. This in turn means that there are few limitations on the variety and number of (metastable) structures which can form. We do see some evidence for destabilization for SiO_2 zeolites having Si-O-Si angles below 140°; the formation of small 3- and 4-membered rings may be energetically limiting to a greater extent than the formation of large pores. This is in accord with the shape of the potential curve for Si-O-Si angles obtained from quantum calculations which shows a small barrier to linearity but a large increase in energy at Si-O-Si angles below about 135°.

Future work on other compositions, especially the Si = Al + Na substitution in different zeolitic frameworks will help clarify the generality of these ideas, as well as providing thermochemical data for important zeolites.

A recent project has opened a new area - that of the energetics of radiation damage in minerals. The enthalpy of annealing of natural zircons as a function of radiation dose shows a plateau at metamictization and the large value of the enthalpy, more than twice the heat of formation from the oxides, is consistent with pervasive damage on the nearest and next-nearest neighbor scale, rather than microcrystallinity. The increase in enthalpy of about 60 kJ/mol could cause a factor of three increase in the equilibrium solubility of ZrO_2 in an aqueous fluid in contact with zircon. Thus damaged zircons are thermodynamically as well as kinetically more reactive. This has ramifications for both radioactive waste disposal and isotope geochronology. We plan to expand this area in future research.

1. Project Title

Thermodynamics of High Temperature Brines
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5. Project Overview

A. Objectives

(1) Discovery and development of equations and methods of calculation and prediction of the thermodynamic properties of high temperature brines of geological significance.

(2) Experimental measurements of key properties required to implement the calculations in (1) which are not being measured elsewhere.

While equations had been known that satisfactorily represented the properties of aqueous solutions with a single solute, these were not conveniently or accurately extendable to mixed solutions (brines) with two or more solutes. For moderate temperatures, theoretically based equations were proposed here in 1973 that proved to be very effective for various properties of mixed brines of any number of components at temperatures up to about 300°C. Mineral solubility calculations on this basis were very successful, and computer codes are now available from USGS, LLNL, and elsewhere. Experimental measurements of properties yielding key parameters were made in this project as well as at ORNL, LANL, the University of Delaware, and elsewhere. This phase is largely complete for major components, but continues, usually in collaboration with groups elsewhere, to obtain parameters for special species of particular interest such as thorium salts.

The primary emphasis recently and in future plans is on systems at near-critical and supercritical temperatures and pressures. Again, relevant statistical mechanical theory is incorporated into practical equations tested first for systems with one component in addition to H_2O. But the extension to multicomponent systems is always considered and is implemented as soon as possible. Often this last step requires new measurements on mixing processes.

The current program is directed primarily toward the system $NaCl-CaCl_2-H_2O$; also to the binary $CaCl_2-H_2O$ in the very concentrated range as an extension of the work at ORNL on more dilute $CaCl_2-H_2O$.

B. Aqueous fluids, brines, play a major role in both natural processes and exploitation technologies of interest to DOE. Hence, a fundamental understanding of these systems is important.

C. As noted in the sections above and from the list of publications, there is close communication and collaboration where appropriate with ORNL and LLNL. That with ORNL is explained above.

5. Scientific and Technical Content

A new heat-of-mixing calorimeter has just been completed and tested. Measurements of the heat of mixing of $NaCl-H_2O$ with $CaCl_2-H_2O$ are proceeding. Initial measurements are being made at moderately high temperatures, 150-200°C, after which measurements will be made at successively higher temperatures. Initially, all measurements will be at about 235 bars pressure, which is above the vapor pressure of pure water; thus, the results can be evaluated for temperature effects at constant pressure.

In parallel with the measurements, a semi-empirical equation of state is being developed for the thermodynamic properties of both the $CaCl_2-H_2O$ binary and the $CaCl_2-NaCl-H_2O$ ternary. For the $CaCl_2-H_2O$ binary there is a good data base up to about 6 molal, and Holmes et al. at ORNL are in the final stages of completion of a comprehensive model. The most recent publication of this project (no. 46) represents the first step in the development of an extension to saturation molality for the aqueous phase, together with the incorporation of the equilibria with the saturating solid phase. This initial step is related to the temperature range 25-100°C. Pertinent data have been assembled and exploratory calculations have been made for the range extending to 250°C. These are encouraging but will not be completed until the final ORNL equation for the range to 250°C and below 6 molal is available. The equilibrium with the saturating phase $CaCl_2 \cdot nH_2O$ is an essential part of the treatment. Another important component is the set of measurements of the vapor pressure of $CaCl_2-H_2O$ at 250°C extending to solid saturation by Ketsko, Urusova, and Valyashko.

On completion of the equation for the $CaCl_2-H_2O$ binary and heat of mixing measurements up to 250°C, work will begin on the modeling of the $NaCl-CaCl_2-H_2O$ ternary. Extension to higher temperatures will follow thereafter, but it is now clear that a different basic formulation of the equation will be required for the ranges above and below 250°C.

7. Project Output

A. The next to last publication, no. 45, "Thermodynamics of Natural and Industrial Waters," summarizes the contributions of this project over a period of several years and the interrelationships of this project with that at ORNL and the University of Delaware. Equations and parameters are now well established for many important components for

the temperature range to 250° or 300°C. It is also explained why different methods are needed for still higher temperatures, and the progress for that range is described.

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Missing Abstract

P.S.Z. Rogers
Thermodynamic properties of aqueous solutions at high temperature and pressure

Development of an Experimental Database and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures.

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We have made measurements of the heat capacity and volumes of aqueous solutions of H_2S, CO_2, CH_4, NH_3, H_3BO_3, and CH_3COOH from 300 to 705 K and pressures near 280 bar. These are nonelectrolyte species of key importance in a large variety of geochemical processes and give us an experimental data base which will allow correlations which can predict other inorganic nonelectrolytes. We are trying various correlations of the data so that we can predict nonelectrolytes, for which no measurements exist. We have found that the equation of Harvey, Sengers, and Tanger is much more accurate in the critical region than that of Shock et al. (1992) If we know the volumes we can quite accurately estimate the heat capacities of these substances. There are also reasonable correlations of the magnitude of the critical effects (both volume and heat capacity) with the critical point of the solute and with Henry's law constant for the solute.

Molecular dynamics simulations of the chemical potential of aqueous methane, ethane, and propane at temperatures from 600 to 1200°C and densities of water from 0 to 1 gm/cm^3 have been made. In connection with this, methods of free energy calculations using molecular dynamic simulations have been developed which improve their accuracy, allow estimation of errors, and decrease the computing time.

We are working on revisions in equations of state for aqueous ions and electrolytes which are widely applicable to geochemical processses. Previous predictions of the properties of electrolytes at high temperatures have relied on the Born model to extrapolate the experimental data. In previous work funded by the National Science Foundation we have developed equations for the model of a hard sphere in a compressible dielectric continuum, and this is expected to be much more accurate than the Born model at high temperaures where the solvent is compressible. The Born model neglects the

compressibility of the solvent. We are currently testing the Born model and the compressible continuum model using 1) experimental data resulting from work sponsored by the National Science Foundation, and 2) Monte Carlo simulations of the chloride ion in water at the following temperatures and water densities: 450½C and 0.01 g/cm^3, 727°C and 0.35 g/cm^3, and 400°C and 0.30 g/cm^{-3}.

We have just finished measurements of the partial molar volume of a variety of organic electrolytes and nonelectrolytes at temperatures from 25 to 325°C. The compounds investigated are: 1-Propanol, Propanoic Acid, Pyridine, 1,4 Butanediol, Propylamine, Adipic Acid, Succinic Acid, Propionamide, 1,6 Hexanediol, 1,4 Butanediamine, 1,6 Hexanediamine, Phenol, Sodium Acetate, Propylamine Hydrochloride, Sodium Propionate, and Sodium Benzenesulfonate. Measurements of the heat capacities of these same compounds will soon be started. These measurements will allow the development of group additivity schemes to predict a very wide variety of organic ions and electrolytes.

A method to estimate values of volumes for aqueous nonelectrolytes at 25°C and 1 bar from critical volumes is being developed.

1. Thermodynamic and Transport Properties of Aqueous Geochemical Systems

Principal Investigator: Joseph A. Rard

Co-principal Investigator: Donald G. Miller

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2. Principal project personnel: Joseph A. Rard

His principle areas of research and expertise are the thermodynamic and transport properties of aqueous electrolyte solutions. This includes experimental determination, data reduction, and interpretation of osmotic and activity coefficients (isopiestic method), Fickian diffusion coefficients (Rayleigh interferometry), solubilities (isopiestic method, isothermal saturation), densities (pycnometry), and electrolytic conductances (ac method). He also does comprehensive critical reviews of chemical and thermodynamic properties of fission-product elements and their inorganic compounds and aqueous species.

Principal project personnel: Donald G. Miller:

His principle areas of research and expertise are in the transport and thermodynamic properties of aqueous electrolyte solutions. This includes experimental determination of Fickian diffusion coefficients (Gouy and Rayleigh interferometry) and electrical conductances (dc method), analysis of diffusion and activity coefficient data, calculation of Onsager transport coefficients and verification of the Onsager Reciprocal Relations, the theory of double-diffusive convection, and equation of state calculations.

3. Project Overview:

A. *Specific Project Objectives*:

1) *Past Objectives:* Our earlier proposal (first funded in 1981) contained the following long-term and short-term objectives: i) systematically explore the composition dependence of (Fickian) diffusion coefficients of representative binary and ternary electrolyte solutions; ii) measure the necessary osmotic/activity coefficients and other auxiliary data to interpret and model transport coefficients for these same systems; iii) use

these and other data to extend available transport coefficient estimation procedures to include higher-valence-type mixtures; and iv) utilize the thermodynamics of equilibrium and non-equilibrium processes to describe complicated mixtures. Systems to be studied were those with radioactive waste isolation, diagenetic, and brine salt applications, including $MnCl_2$-H_2O and NaCl-$SrCl_2$-H_2O at 25°C.

Most of the above objectives were accomplished: our diffusion coefficient, density, and osmotic/activity coefficient data for $MgCl_2$-H_2O and $MnCl_2$-H_2O have been published. Diffusion coefficients and densities have also been published for NaCl-$SrCl_2$-H_2O, as have part of the osmotic/activity coefficient data. We measured and published an extensive amount of these types of data for the ternary sea water analogue NaCl-$MgCl_2$-H_2O at 25°C, and extensive isopiestic measurements for the system Na_2SO_4-H_2SO_4-H_2O, which is the first acidic sulfate system to be thoroughly characterized. A considerable effort was expended on modeling diffusion coefficients of the mixed electrolytes NaCl-$MgCl_2$-H_2O and NaCl-$SrCl_2$-H_2O. Diffusion coefficient measurements were made for the geochemical systems KCl-H_2O, $NaHCO_3$-H_2O, and $KHCO_3$-H_2O, for the waste isolation system NaI-H_2O, and for the toxic-metal system $BaCl_2$-H_2O; isopiestic measurements for the waste isolation system NaCl-CsCl-H_2O; and both of these properties and densities for the waste isolation systems CsCl-H_2O and $SrCl_2$-H_2O and the toxic-metal system $CdCl_2$-H_2O, all at 25°C. We organized and participated in an international collaboration to characterize experimentally the transport and thermodynamic properties of NaCl-$MgCl_2$-H_2O.

In addition, major advances were made in understanding double diffusive convention, and equations were derived for calculating diffusion coefficients for four-component systems from Rayleigh and Gouy interferometric data. The case of equal eigenvalues in the diffusion coefficient matrix was successfully investigated.

2) *Current Objectives*: Our new proposal (funded in October 1992) contained the following long-term and short-term objectives: i) to measure highly-precise osmotic/activity coefficient data over the full composition range by the isopiestic method for $MgSO_4$-H_2SO_4-H_2O and NaCl-$CaCl_2$-H_2O at 25°C; ii) measure Fickian diffusion coefficients for K_2SO_4-H_2O at 25°C with Rayleigh interferometry; iii) measure diffusion coefficients for NaCl-Na_2SO_4-H_2O at 25°C by Gouy or Rayleigh interferometry; iv) begin diffusion coefficient measurements at higher temperatures; v) complete the calculation of the generalized transport coefficients for NaCl-$MgCl_2$-H_2O as part of the international collaboration; and vi) extend the data analysis methods and estimation procedures for ternary systems as necessary to analyze our experimental data.

These particular systems were chosen for the following reasons. Pitzer's equations have proven to be the most useful and frequently the most accurate for modeling osmotic and activity coefficients and solubilities of highly soluble electrolytes. We chose $MgSO_4$-H_2SO_4-H_2O and NaCl-$CaCl_2$-H_2O for study because of their highly non-ideal behavior and high solubilities and because they are presently inadequately characterized. These data will challenge the ability of Pitzer's equations to model such non-ideal and extremely soluble systems. Diffusion measurements are being done for K_2SO_4-H_2O to complete measurements for all binary subsystems formed from Na-K-Ca-Mg-Cl-SO_4-H_2O, and thus will allow these mixtures to be modeled by the approach of Felmy and Weare (*Geochim. Cosmochim. Acta* (1991) **55**, 113-131 and 133-144). Diffusion measurements are being done for the common cation system NaCl-Na_2SO_4-H_2O because preliminary results from our laboratory indicate that at least one cross-term diffusion coefficient is negative. This is in dramatic contrast to our results for common anion (chloride) systems where both cross-term coefficients are positive and usually large. One system previously studied (NaCl-$MgCl_2$-H_2O) is also a subsystem of Na-K-Ca-Mg-Cl-SO_4-H_2O, for which ternary diffusion data are essential for testing estimation procedures for mixtures.

We have begun isopiestic measurements for $MgSO_4$-H_2SO_4-H_2O, along with new measurements for H_2SO_4-H_2O and $MgSO_4$-H_2O at low molalities and $CaCl_2$-H_2O at high molalities (where literature data are somewhat discrepant). Also, we have finished and published the last of five papers giving diffusion data for NaCl-$MgCl_2$-H_2O; that paper also contains a comprehensive discussion of the data measurement method, photographic plate reading, and calculation methods for Rayleigh interferometry. Relations between refractive index and density are being explored, and may yield results that will allow more accurate corrections for skewing of fringe patterns at low concentrations.

3) *Planned Future Work*: During the remaining three years plus of this project, major emphasis will be on completing the experiments and calculations described in the first paragraph of the preceding subsection "Current Objectives." In addition, we have longer range goals which include: i) Perform isopiestic measurements for some extremely soluble quaternary systems (three electrolytes in water) to provide a rigorous test of the ability of Pitzer's equations to predict properties of such mixtures from ternary solution parameters. ii) Develop equations and computer programs for analysis of diffusion data for five-component systems. iii) Measure diffusion coefficients of the remaining (minor) brine salts, carbonates and bromides. iv) Measure diffusion coefficients at several compositions of Na_2SO_4-$MgSO_4$-H_2O, $MgCl_2$-$MgSO_4$-H_2O, and NaCl-Na_2SO_4-$MgSO_4$-H_2O to test Young's cross-square rule. If this rule is found to be obeyed, it will allow estimation of transport coefficients for systems with any number of components.

B. *Relation of this Project to the DOE Mission:*

According to *Summaries of FY 92 Geosciences Research*, the Geosciences Research Program is "directed towards the long-term fundamental knowledge base necessary to provide for energy technologies of the future." Also stated was that this knowledge is to be sought for processes related to "(1) the energy and mineral resources of the Earth and (2) the energy byproducts of man." Most of our research falls into this category,

Many of our previous osmotic coefficient, solubility, and diffusion measurements were devoted to systems with application to nuclear waste isolation, and thus with the safe disposal of byproducts of nuclear energy. Our recent interest in the thermodynamics of mixed electrolytes containing high concentrations of sulfuric acid is because of their presence in atmospheric aerosols and acidic mine waste. Thus these data can help us understand problems arising from combustion of fossil fuel and from extraction of minerals. Our thermodynamic activity and diffusion coefficients for binary and ternary systems of brine salts can help understand the diagenetic sequences during evaporite formation and dissolution, and thus help plan the efficient utilization of mineral resources.

C. *How this Project is Related to Other Projects Being Funded by DOE:*

The isopiestic measurements are being done for various brine salts, their mixtures, and for acidic sulfate mixtures, all at 25°C. These data extend from low molalities up to saturation or supersaturation. When our results are coupled with other thermodynamic data such as enthalpies of dilution, heat capacities, and/or high-temperature isopiestic measurements, the resulting equations yield reliable values of thermodynamic quantities such as activity coefficients, water vapor pressures, and solubilities at various temperatures and salt ratios. The *Summaries of FY 92 Geosciences Research* indicate that Ken Pitzer at University of California, Berkeley and Pam Rogers at Los Alamos National Laboratory are measuring enthalpies of dilution and heat capacities of various brine salts and their mixtures at high temperatures. H.F. Holmes and R.E. Mesmer at Oak Ridge National Laboratory are doing high-temperature isopiestic measurements for various electrolytes and their mixtures and J.M. Simonson is doing high-temperature enthalpy of dilution measurements, with support from OBES/Chemistry and other DOE sources. Our measurements complement the others, since some electrolytes have been studied by several of these groups. There has been a free exchange of thermodynamic data between LLNL, ORNL, and Berkeley.

Our diffusion and transport property measurements also have their counterparts in the OBES/Geosciences programs. These include the high-temperature reactive transport

modeling efforts of A.C. Lasaga at Yale University and H.C. Helgeson and C.L. Carnahan at Berkeley. There is a particularly strong overlap in interest with J.H. Weare (non-OBES funded research) at the University of California, San Diego. He has previously modeled our diffusion coefficients for brine salts, based on an application of Pitzer's activity equations and extensions of our earlier transport models to non-common ion mixtures.

4. Scientific and Technical Content:

A. *Relation of this Research to Research Being Conducted by Others in the Field:*

In section 3.C we describe how our project is related to others funded by DOE. We will now very briefly describe how our research is related to others in the field.

In the USA isopiestic measurements are currently being done Don Palmer, H.F. Holmes, and R.E. Mesmer at ORNL; O.D. Bonner at University of South Carolina (Columbia); and J.G. Albright at Texas Christian University. Bonner has not studied geochemical systems, and Albright has just started this research. Palmer has studied several geochemical systems from 25 to 50°C, but none of his results are published. Holmes and Mesmer are the only group that operate at 110°C and above, and have studied many geochemical systems. One group in Scandinavia does measurements at 100.3°C, but not for geochemical systems. Our measurements and those of Holmes and Mesmer and Palmer complement each other, and when combined with enthalpy and heat capacity measurements by Ken Pitzer (Berkeley), Pam Rogers (Los Alamos), Mike Simonson (ORNL), and Bob Wood (University of Delaware), provide thermodynamic results from 25°C to the critical point of the solutions.

We already mentioned the relation of our diffusion measurements to transport modeling in 3.C and will not repeat that information. The only other groups that measure precise Fickian diffusion coefficients are those headed by John Albright (Texas Christian), V. Vitagliano (Naples, Italy), and Derek Leaist (University of Western Ontario, Canada). Leaist does not use optical interferometry. The Naples group studies few geochemical systems but collaborated with us on the study of NaCl-$MgCl_2$-H_2O. Leaist also collaborated by doing dilute solution measurements for NaCl-$MgCl_2$-H_2O. Albright has worked extensively with us in the past, and this collaboration continues.

B. *Schedule of Major Research Activities:*

It is difficult to make realistic predictions as to when our research goals will be accomplished, because the number of experiments depends on "circumstances beyond our control." For example, the number of diffusion experiments required for a ternary

composition can be as few as four. However, if gravitational instabilities occur, as found for two compositions of $NaCl-SrCl_2-H_2O$ (Rard and Miller,1988), then several additional experiments are required. Likewise, additional experiments are necessary if the eigenvalues of the diffusion coefficient matrix are nearly equal. The number of isopiestic experiments varies with the molality range; both $MgSO_4-H_2O$ and $CaCl_2-H_2O$ exhibit a considerable tendency to supersaturate, which is likely to be the case for their ternary solutions.

Based on previous experience we anticipate the isopiestic experiments for $CaCl_2-H_2O$ will be finished by the end of 1993, for $MgSO_4-H_2O$ and $H_2SO_4-H_2O$ by the end of 1994, and for $MgSO_4-H_2SO_4-H_2O$ by the end of 1995. We hope to finish diffusion experiments for $K_2SO_4-H_2O$ by the end of 1994, and for $NaCl-Na_2SO_4-H_2O$ by the end of 1995. The time for completion of calculations of transport coefficients for $NaCl-MgCl_2-H_2O$ can not be predicted, because they depend on transference number measurements being done by Schönert and co-workers in Aachen, Germany.

C. *Scientific/Technical Issues Currently Being Addressed and Their Significance*:

There are numerous geochemical, chemical, industrial, biological, atmospheric, and metallurgical systems involving aqueous mixed electrolytes. In many cases these solutions are quite concentrated, which makes their thermodynamic and transport properties more difficult to predict. Thermodynamic activity data are needed for predicting optimum conditions for purification of salts by fractional crystallization, the diagenetic sequences observed during evaporation of sea water or brines, the conditions for growth of sulfuric acid atmospheric aerosols, and the interaction of radioactive waste with bedded salt. Diffusion coefficients are needed for understanding and quantifying certain dissolution/precipitation reactions, for calculating mass-balance relations for saline lakes and oceans, for modeling reactive transport, for modeling transport away from waste repositories, and many other cases.

The reliable prediction of activities and solubilities of electrolytes in concentrated solutions has become commonplace due to the use of Pitzer's equations as recommended by Harvie and Weare (Geochim. Cosmochim. Acta (1980) 981-997). However there are some mixtures of extremely soluble electrolytes for which thermodynamic modeling has been considerably less successful, such as solutions of $CaCl_2$ and H_2SO_4. Even though available methods for predicting diffusion coefficients and Onsager coefficients of mixed electrolytes are well-developed and reliable for mixtures of 1-1 salts, they still need to be extended to include mixtures of higher-valence salts.

Given the considerable number of electrolyte mixtures of scientific interest, it is obviously impractical to measure thermodynamic and diffusion data for all or even most of them. Therefore, our goal is to accurately and thoroughly characterize properties of several representative systems, and then concentrate our efforts on using those results to develop reliable estimation methods for mixtures. For activity coefficients we are studying acidic sulfates and NaCl-$CaCl_2$-H_2O, which show considerable solubility and are difficult to model with the usual activity equations. For diffusion we will study the common-cation system NaCl-Na_2SO_4-H_2O, which has a negative cross-term coefficient. Our previous studies for chloride mixtures showed only positive (frequently large) cross terms.

D. *Experimental and Theoretical Approaches, Techniques Used, Resources Applied*:

Our thermodynamic osmotic/activity coefficient measurements and solubilities are being done by the isopiestic vapor-pressure method. These measurements are relatively straightforward for aqueous solutions around room temperature, and can be highly accurate when properly done (Rard and Platford, 1991). This method is particularly convenient when large amounts of data are required to characterize electrolyte mixtures. We have three chambers designed for operation around 25°C, along with a constant temperature bath and necessary auxiliary equipment.

The most accurate methods for measuring Fickian diffusion coefficients of liquid solutions are based on optical interferometry (Miller and Albright, 1991). We have a Rayleigh interferometer at LLNL, and have ready access to the world's-finest diffusiometer at Texas Christian University. Comparators are available for reading photographic records of the experiments, as are computer programs for analyzing these data.

Our isopiestic data are being analyzed by Pitzer's equations with inclusion of higher-order electrostatic effects. Based on our experience with Na_2SO_4-H_2SO_4-H_2O (Hovey, Pitzer, and Rard, 1993), some additional modifications of Pitzer' equations may be required because of the extremely high molalities involved. Our diffusion coefficients and other transport data are being analyzed as Onsager transport coefficients within the framework of irreversible thermodynamics, which provides much insight into transport processes and which can be used for estimating properties for mixtures.

E. *Importance of Solving the Problem Being Addressed by the Research*:

Aqueous electrolyte solutions are pervasive in numerous fields in addition to geosciences. Characterizing their thermodynamic and transport properties is critical for modeling and understanding chemical changes during reactive transport, solubility and precipitation behavior in brines, transport of radioactive waste from a breached repository,

formation of atmospheric aerosols, extractive metallurgy, transport of solutes through membranes, transport in solar ponds, and the variations of concentrations of ions in estuarine and oceanic sediments. Such information will allow the optimization of certain chemical processes and help understand and alleviate problems arising from utilization of current energy technologies (such as the fate of SO_3 in the atmosphere).

We are experimentally studying thermodynamic activities and diffusion for systems of high scientific interest, which are not now predictable or reliably modeled. It is expected that efforts to model the resulting behavior will lead to significant extensions and improvements upon theory and modeling equations currently being used. They will thereby improve estimation methods, and thus may greatly reduce the number of experiments required to characterize important electrolyte mixtures.

5. Project Output:

A. *Major recent accomplishments (during the last two years):*

i) We have written comprehensive state-of-the-art reviews of the isopiestic method (Rard and Platford, 1991) and optical diffusion methods (Miller and Albright, 1991); both were published as book chapters. 2) We published the last paper of our detailed study of the diffusion of NaCl-$MgCl_2$-H_2O at 25°C (Miller, Albright, et al., 1993). These data provide a high-quality data base for testing theories and estimation methods for multicomponent transport properties. 3) We published our detailed study of osmotic and activity coefficients of Na_2SO_4-H_2SO_4-H_2O at 25°C (Rard, 1992; Hovey, Pitzer, and Rard, 1993). These data have direct applications to the thermodynamic analysis of atmospheric sulfuric acid aerosols and acidic mine liquids. 4) We helped prepare computer programs for extracting the nine diffusion coefficients of four-component systems and tested them on diffusion experiments done at the University of Naples (Paduano, Sartorio, et al., 1992). This is the first set of diffusion coefficients for a four-component system from optical interferometry.

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* This project has been funded since FY1979 and has produced 52 formal publications from work entirely or partially supported by OBES Geosciences, and several papers have been presented at scientific meetings. Only those from 1985 to the present are given. A full listing is available upon request.

Abstract Submitted to

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Three-Dimensional Imaging of Drill Core Samples Using Synchrotron Computed Microtomography

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Computed tomography using x-ray tube sources has been pursued extensively for examination of drill core samples. The work has been done at both universities and at many petroleum companies. In general, the spatial resolution has been relatively poor although industrial x-ray units exist which can make measurements with voxel sizes $\leq$ 10,000 μm^3. Magnetic resonance imaging has also been used at about the same resolution level.

The synchrotron x-ray source is particularly useful for high resolution studies that are not feasible with optical microscopy or other conventional methods. This is evidenced by the fact that a number of petroleum companies have used the X26 x-ray microscopy facility for tomography experiments. These companies include Amoco, Mobil, ELF-Acquitaine, and BP. Exxon also operates a microtomography facility at the Brookhaven National Synchrotron Light Source (NSLS) specifically for proprietary work. The X26 projects helps to open the world of synchrotron microtomography to other companies.

The present work is mainly carried out using x-rays produced at a bending magnet beam line at the NSLS which can be used at x-ray energies up to roughly 30 keV. In addition, work at higher x-ray energies is done at a superconducting wiggler beam line which produces useable beams with energies in excess of 100 keV. The CMT apparatus is modular in design so that different types of x-ray detectors can be easily used. Most of the work has been done using first-generation tomographic methods with a pencil beam of x-rays. This method has definite advantages in that it can be used for high resolution work by simple collimation of the incident x-ray beam. Hence, spatial resolution is not limited by the x-ray detection system. Fluorescent emission tomography is possible if an energy-dispersive spectrometer is used for detection of characteristic x-rays from the sample.

This apparatus is now being used for investigating the microgeometry of rocks. The measurements include test work on a volume of 100 μm diameter glass beads, and measurements on Berea and Fontainebleau sandstones, and Dania chalk. Measurements on large specimens of Nugget and Cozette sandstone, siltstone, volcanic tuff, and silica/quartz from Middle Ground Shoals, Alaska. The tomograms reveal individual grains, porosity, inclusions of different densities, and cracks.

The experimental data is analyzed using 2-point correlation functions in order to obtain quantitative information on porosity, specific surface area, and particle sizes and distributions. Different components of the materials can be investigated by setting a window on specific values of the measured linear attenuation coefficients. Work is also in progress to develop analytical methods that provide statistical descriptions of

the distribution of pore size, throat size, and pore connectivity. In addition, the experimental data is being used by several other groups working with different models for their use. A comparison of the results from the different theoretical approaches should help to bring about improved computational methods.

Adequate visualization is an important tool in interpretation of the tomographic data. Some time has been spent on working with A. Kaufman and his students in adapting his medical visualization software, Vol-Vis, for display of the geological tomographic images. This software facilitates changing the region of the sample which is displayed and the degree of magnification. This software has been used for visualization of several of the samples.

There is a strong need to further improve the tomographic hardware so as to obtain reduced imaging times and better spatial resolution. It is planned to install an x-ray detection system based on a charge-coupled device (CCD) camera for making images of volumes with 10^3 voxels. This camera will make it feasible to drastically increase the rate at which specimens can be examined with 20-30 μm resolution. Methods for obtaining high spatial resolution must be devised as well.

As a result of the work described here, it was realized that it is now possible to build advanced tomographic apparatus which will make possible real-time computed tomography (RTCT) that will drastically reduce data acquisition times. This equipment will merge new x-ray sources (Argonne National Laboratory Advanced Photon Source, for example) high speed CCDs, and massively parallel computer systems in order to obtain volume images of 512^3 voxels at a rate of 10-15 Hz with voxel sizes approaching 1 μm^3. A workshop on the scientific applications of such an instrument was held on May 19, 1993 at the NSLS Annual User Meeting. We presently work on further development of the RTCT concept.

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FUNDAMENTAL RESEARCH IN THE GEOCHEMISTRY OF GEOTHERMAL SYSTEMS

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Aluminum speciation and equilibria in geothermal brines

Permeability is one of the most important features of geothermal and geopressured systems, controlling fluid flow to the reservoir, the amount of and rate at which energy can be extracted, and the seal which maintains reservoir integrity. In volcanic (geothermal) and sedimentary (geopressured, geothermal) settings, aluminosilicates such as feldspars, clays and micas, often precipitate or dissolve during the evolution of the systems. This can create or destroy permeability. The stability of aluminosilicate phases also controls, to a large extent, the chemical composition of the geothermal fluid. Brine chemistry is currently of great interest in the geothermal community, because of problems encountered with scaling (mineral precipitation) and corrosion in the Geysers and Salton Sea geothermal fields.

A major obstacle to the quantitative modeling of brine chemistry and mineral stability in fluid/rock interaction systems has been uncertainty as to the speciation and thermodynamic properties of aluminum. This element occurs in Earth fluids as species of the form $Al_x(OH)_y^{3x-y}$, where species with (x,y) stoichiometries of (1,0) or Al^{3+} to (13,32) a complex polynuclear ion. The formation of polymeric aqueous species is sluggish, as is the dissolution and precipitation of aluminum minerals. These factors have greatly hampered experimental efforts to determine the relevant speciation and true aluminum mineral solubilities in long-lived geologic environments. The aluminum ions can themselves form complexes with other solution species, further confusing interpretations.

In order to resolve these issues, we have undertaken a detailed study of the monomeric speciation of aluminum in NaCl brines by measurements of the solubility of gibbsite -- $Al(OH)_3$ -- and potentiometric titrations of Al^{3+}. The results of this work have broad applications in other geologic settings relevant to the DOE mission, such as hydrocarbon migration and accumulation and waste disposal.

Well characterized and carefully pretreated (to remove metastable surface phases and features) synthetic gibbsite (Alcoa C-31) was equilibrated with aqueous solutions in disposable polypropylene syringes in a rotating rack (6 revolutions per hour) which was suspended in a thermostatted water bath for experiments from 6 to 80°C (±0.01°C). The solid was allowed to equilibrate for periods of weeks to many months, depending on temperature and pH. Samples were periodically withdrawn through fluorocarbon syringe filters and the samples analyzed for total aluminum by ion chromatography. New techniques were developed for quantitative chromatographic analysis of aluminum in the ppt to sub-ppb range. The *in situ* pH of each sample was measured at the end of each run.

The experimental results in 0.001 to 5.0 molal NaCl+HCl solutions, in which Al^{3+} is the dominant species, are shown in Fig. 1, expressed as the equilibrium quotient $Q = mAl^{3+}/(mH^+)^3$. At each temperature and ionic strength, five different starting H^+ concentrations (0.001 to 0.02 molal) were used. Fig. 2 shows the results of experiments in NaCl+NaOH (0.01 and 0.1 molal NaOH, diamonds) and NaOH (inverted triangles) where $Al(OH)_4^-$ is the dominant species, expressed as the equilibrium quotient $mOH^-/mAl(OH)_4^-$. The slight difference between the values in

Fig. 1

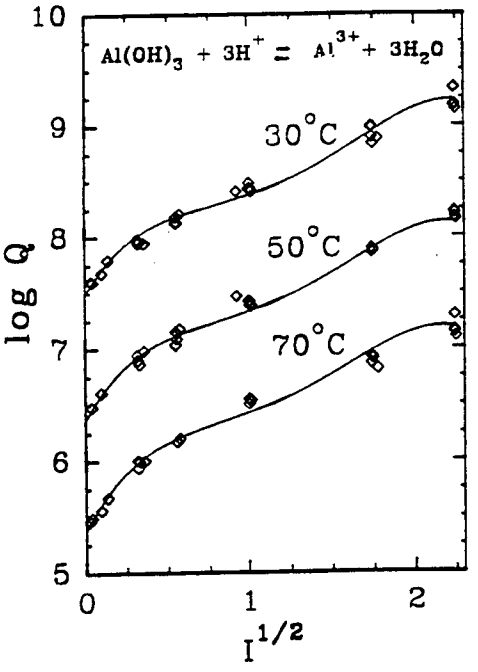


Fig. 2

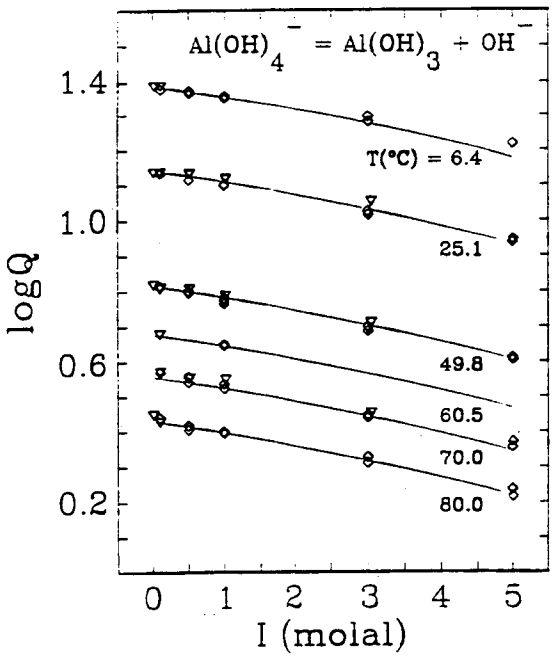


Fig. 3

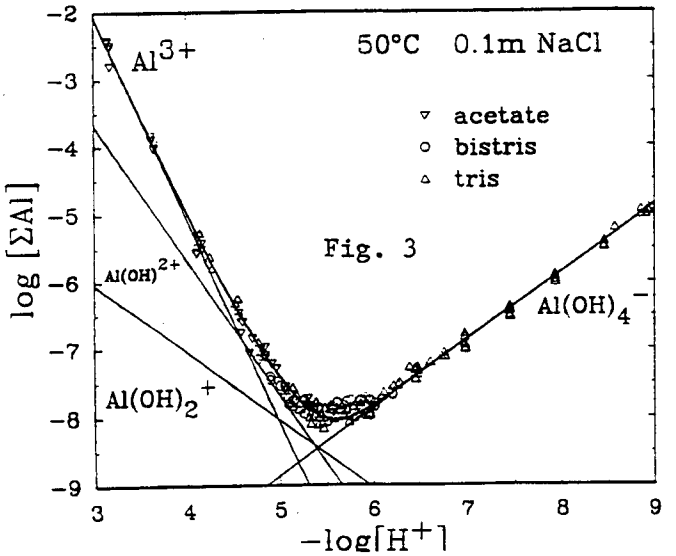


Fig. 4

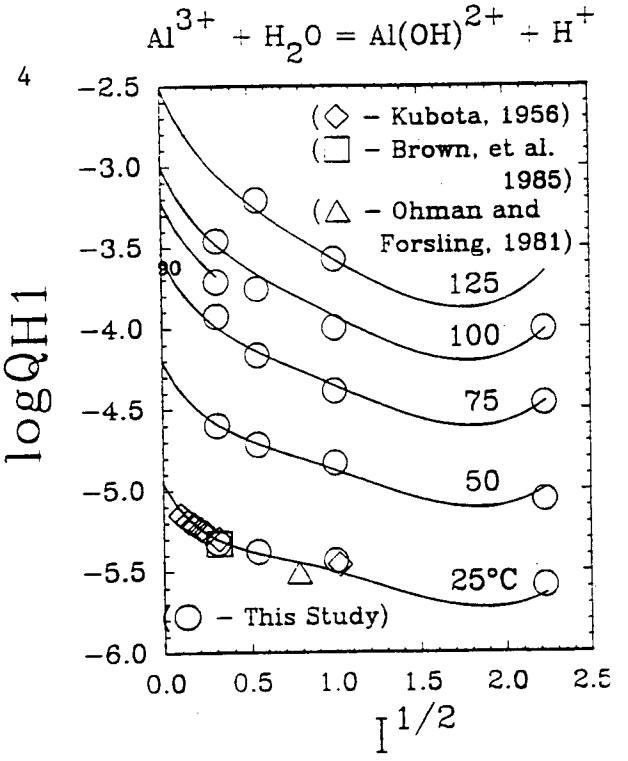


Fig. 5

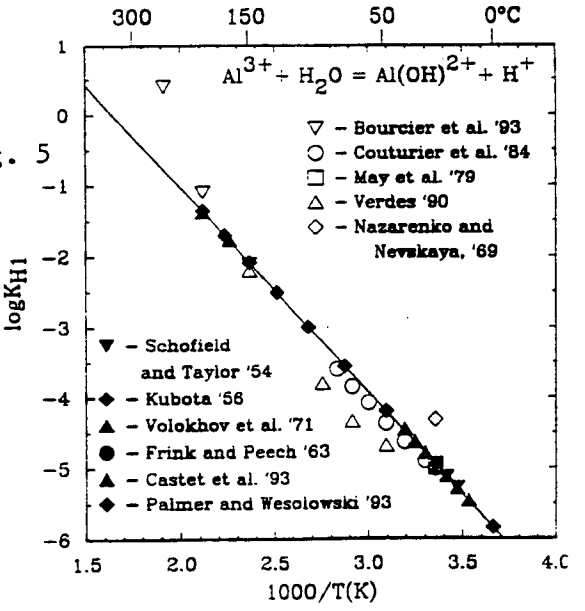
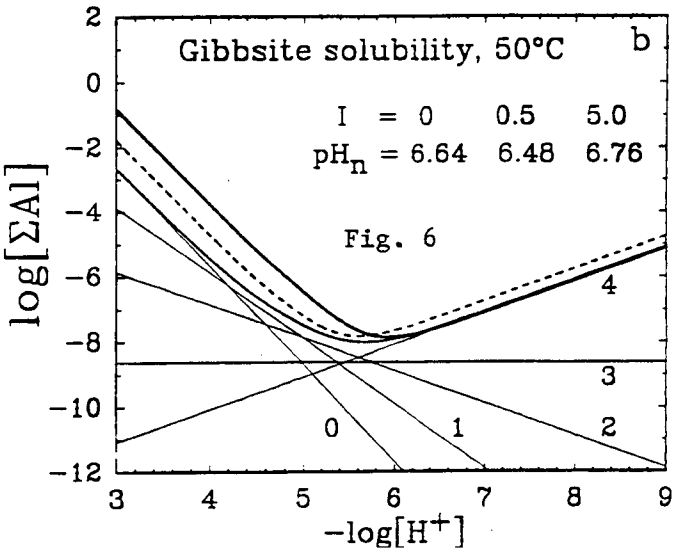


Fig. 6



chloride versus hydroxide media (spanning many orders of magnitude in total aluminum concentration) are due to specific ion interactions. From the results of these two studies, we were able to determine the thermodynamic properties and activity coefficients of Al^{3+} and $Al(OH)_4^-$ from 0 to 100°C and 0-5 molal in NaCl brines.

Gibbsite solubility was next measured at 50°C and 0.1 molal NaCl at pH's (defined throughout our work as pH ≡ -log(mH^+)) of 3 to 9 in acetate, bistris and tris buffers. These buffers were chosen because previous work at 25 and 50°C in the same buffers had given solubilities much higher at pH 3 and 9 than we predicted from the data in Fig.s 1 and 2, and a discontinuity of 0.5 to 1.5 log units was reported at pH 7. We discovered that acetate complexes Al^{3+} much more strongly than has been previously known and we have, in another BES/Geosciences project, quantitatively determined the stability constants of $AlAc_y^{3-y}$ species by potentiometry. Bistris was also found to complex $Al(OH)_4^-$ and the stability constant for the complex was determined by solubility and Raman spectroscopy as a part of this project. After correcting for the acetate and bistris complexes, the solubility curve was obtained which is shown in Fig. 3., defined by 184 experimental values obtained after 35, 63, 66, 120 and 144 days equilibration.

A study of Al^{3+} hydrolysis in 0.1 to 5.0 molal NaCl to 125°C by potentiometric titrations in a hydrogen-electrode concentration cell was performed in parallel with the solubility studies. The results, together with the relevant literature data are shown in Fig.s 4 and 5 as the equilibrium formation quotient for $Al(OH)^{2+}$ in brines (Q_{H1}) and pure water(K_{H1}). In Fig 3, the concentrations of Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_4^-$ in equilibrium with gibbsite at 50°C and 0.1 molal NaCl calculated from the results discussed above are plotted as the straight lines. These perfectly match the solubility data, except at pH 5-5.5, were an additional species was needed. Modeling of the solubility curve with the results above enabled extraction of the solubility product for $Al(OH)_{3,cr} + H^+ \rightleftharpoons Al(OH)_2^+ + H_2O$, equal to $10^{-3.04\pm0.05}$. The contribution of $Al(OH)_2^+$ to the solubility is shown in Fig. 3 and the heavy curved line running through the data points is the computed total solubility due to all of the species discussed above. Deviation of the measured solubilities from this curve is at worst, ±0.2 log units, even at sub-ppb levels.

Fig. 5 indicates that we are in exact agreement with the formation constant for $Al(OH)^{2+}$ derived by CASTET et al. (1993) from boehmite solubility measurements. In fact, the attached manuscript by Wesolowski and Palmer (1993) demonstrates that all of our derived speciation and solubility measurements are in agreement with Castet's work. The data in Fig. 3 provided a powerful constraint in extrapolating Castet's data to low temperature. From this analysis, a model has been developed which a.) completely describes the speciation of aluminum and the solubility of gibbsite in 0-5 molal NaCl brines from 0 to 100°C, the conditions commonly encountered in geopressured systems and geothermal recharge zones; and b.) gives greater reliability to calculations of aluminum speciation and mineral solubilities in the 100-350°C range at low ionic strengths. Fig. 6 shows the distribution of species $Al(OH)_y^{3-}$ for y= 0 to 4 at infinite dilution (light straight lines), and the total aluminum in solution at infinite dilution (light solid curve), 0.5 molal (dashed curve) and 5.0 molal NaCl (heavy curve). As can be seen, at pH's 1 to 2 log units more acid than neutral, the solubility of gibbsite, and of any other aluminum phase, is highly dependent on both pH and total salinity. $Al(OH)_4^-$ is always the dominant aluminum species at neutral pH, at all conditions of temperature and salinity.

Salt effects on oxygen and hydrogen isotope partitioning between geothermal brines and vapor

It has long been known that, at room temperature, the vapor over solutions of strong electrolytes has D/H and $^{18}O/^{16}O$ ratios which are different from the vapor over pure water of the same isotopic composition, and that the salt effects on isotope partitioning, defined as

$$10^3 \ln\Gamma = 10^3 \ln(R^v_{salt}/R^v_{pure}) \simeq \delta^v_{salt} - \delta^v_{pure}$$

where R^v is the heavy to light isotope ratio of the vapor over either pure water or a salt solution of the same water, are linearly related to the salt molality. It is presumed that these effects are a measure of the "activity/concentration ratios"of the isotopic waters. As such, any separate phase or species, such as a mineral or a gas in the vapor phase, should also respond to changing salinity of a coexisting aqueous solution. Truesdell (1974) and Poulson et al. (1991) (see discussion in the attached preprint by Horita et al., 1993) reported oxygen isotope salt effects at high temperature (>100°C), which vary widely with temperature and salinity, showing reversals in trends. Because of the unusual T-X dependencies reported at high temperatures, few isotope geochemists have incorporated salt effect corrections into their calculations.

In geothermal systems, the hydrogen and oxygen isotope compositions of steam, brines and alteration minerals are widely used in determining fluid sources and fluxes, reservoir temperatures, extent of boiling, and the time-temperature evolution of a given system. Therefore, because some systems are highly saline throughout (e.g. Salton Sea) and many systems experience boiling and salinity increases, it is important to quantify the effect of salts on isotope partitioning in these systems.

Our approach in studying this system has been to work from room temperature, where there is broad agreement on the slope and sign of salt effects, to high temperatures where there is much confusion. We first constructed a set of 8 glass vessels in which a magnetically-stirred brine is allowed to equilibrate with two separate vapor volumes, each of which can be isolated from the liquid by closing teflon valves at the experimental temperature. A two-tier bath keeps the vapor volumes slightly higher in temperature than the liquid reservoir. With this apparatus,. we have measured the oxygen and hydrogen salt effects of 0.5-6 molal NaCl, 0.5-4 molal KCl, 0.5-5 molal $MgCl_2$ and $CaCl_2$, and 0.5-2 molal Na_2SO_4 and $MgSO_4$ from 50 to 100°C. The hydrogen isotope salt effects are shown to be in quantitative agreement with the work of Kakiuchi (1990), who used an H_2 equilibration method rather than vapor sampling, and with nearly all reported oxygen and hydrogen isotope salt effects reported at room temperature. For all salts, the observed effects increase linearly with salinity and decrease slightly with increasing temperature. Figures 7 and 8 give representative data at 100°C for a number of salts. Details are presented in the attached preprint by Horita et al. (1993). As can be seen, the effects are large and obviously geologically significant.

For work in the 100-200°C, we built 6 stainless-steel pressure systems with a two-tier furnace and vapor spaces isolatable by remotely-actuated bellows valves, much like the glass system. With this system, we have measured the hydrogen and oxygen isotope effects of 0.5 to 5.0 molal NaCl from 100 to 200°C. Finally, we are now using a dynamic vapor sampling apparatus developed with

support from the Geothermal program (and being used for HCl volatility studies) to measure the effects of NaCl to 350°C.

Using all three types of experiments, we have measured the pure water liquid-vapor partitioning of both oxygen and hydrogen isotopes. The hydrogen isotope partitioning is in complete agreement with all previous studies, which employed a variety of methods. However, as shown in Fig. 9, our measured oxygen partitioning is somewhat lower than previously accepted values in the 100 to 250°C range by 0.5 to 1.0 per mil. Our results are in much better agreement with calculations based on vapor pressure ratios of $H_2{}^{18}O$ and $H_2{}^{16}O$ and may be an improvement over the currently-used fractionation factor for this important equilibrium.

As at low temperature, the oxygen isotope salt effect of NaCl solutions is near zero (± .3 per mil) to 200°C at all salinities and to 350°C at 1.0 molal NaCl, as shown in Fig. 10. The plot also shows the temperature trends reported previously. It is suggested that previous studies may have suffered from experimental problems, or with interpretation of data obtained by sampling CO_2 gas equilibrated with the brine (Truesdell, 1974) or by precipitating barium carbonate from solution (Poulson et al., 1991), rather than the direct vapor sampling approach employed in this study. The effect of NaCl on D/H partitioning at temperatures of 100 to 350°C is only slightly less than that shown at 100°C in Fig. 7. We expect the large negative oxygen isotope salt effects observed for divalent salts and large positive hydrogen isotope salt effects of the alkaline earth chlorides (Fig. 8) to persist to high temperatures as well. From these observations, we conclude that the isotope salt effects are very significant in the interpretation of isotope systematics in saline brines at elevated temperatures, but that they are very different from effects reported in the past.

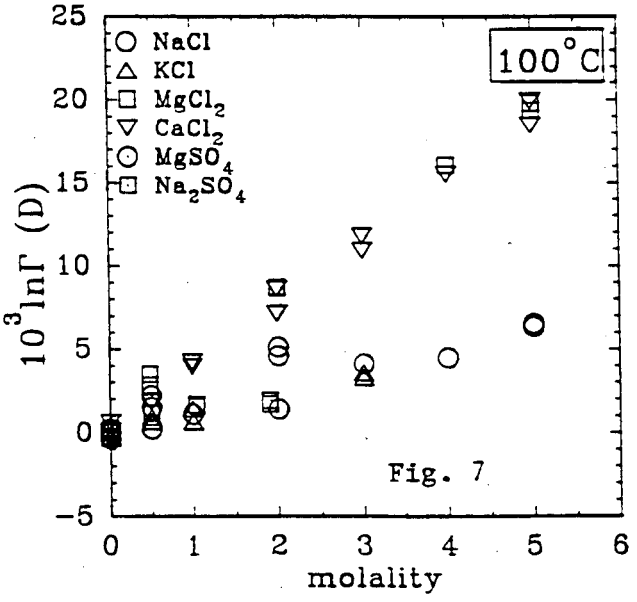


Fig. 7

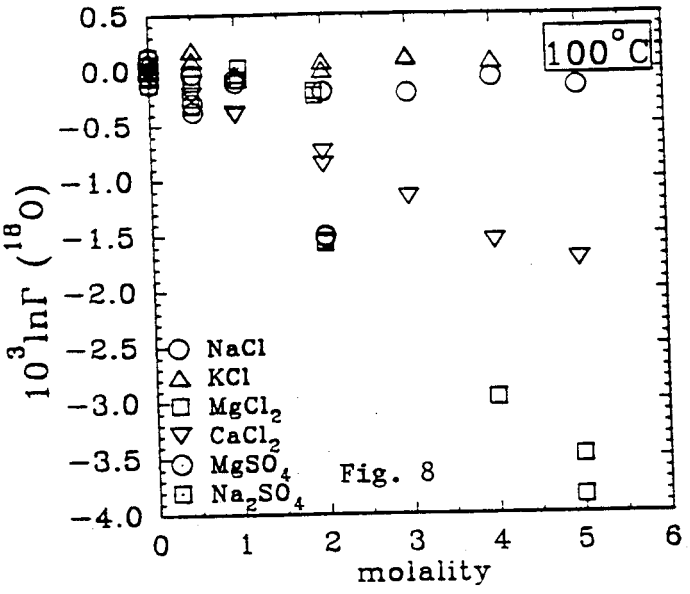


Fig. 8

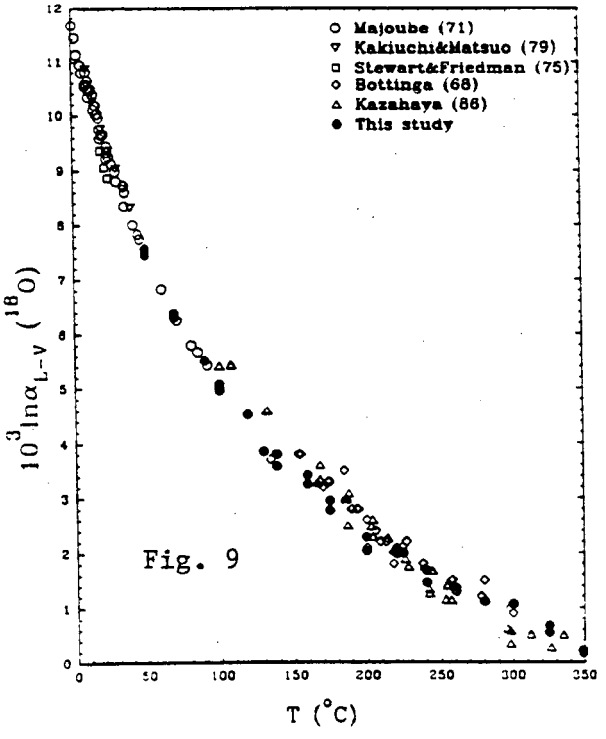


Fig. 9

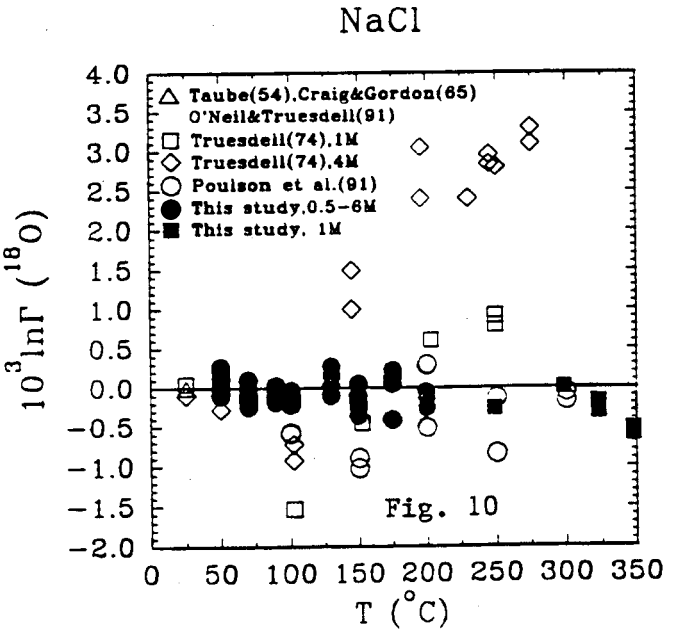


Fig. 10

Major Accomplishments

1. Gibbsite solubility was measured in NaOH, KOH, and NaCl-NaOH solutions ranging from 0.01 to 5.0 molal at 6-80°C, with a reversal at 50°C. The results were coupled with literature data and modeled from 0-100°C to 12 molal ionic strength.

2. Gibbsite solubility was measured in 0-5 molal NaCl solutions containing 5 different HCl concentrations (0.001 to .02 molal) at each ionic strength (0.1, 0.5, 1.0, 3.0 and 5.0).

3. The formation constants for the reaction $Al^{3+} + H_2O = Al(OH)^{2+}$ were measured by potentiometric titration in a hydrogen-electrode concentration cell from 25 to 125°C in 0.1 to 5.0 molal NaCl solutions.

4. Gibbsite solubility was measured (184 points) at 50°C and 0.1 molal NaCl in buffers (acetate, tris, bistris) over the pH range of 3 to 9. Al^{3+} was found to be complexed by acetate and $Al(OH)_4^-$ by bistris.

5. The interaction of aluminate with bistris and acetate were quantified and a "noncomplexed" solubility curve established with a minimum near 10^{-8} molal total aluminum at pH 5.5. The formation constant for the species $Al(OH)^{2+}$ was extracted from these results, in combination with the results above.

6. All of the results above, together with recent literature data on the solubility of boehmite in dilute aqueous solutions at 90-350°C have been incorporated into a general model of the speciation of aluminum from 0-350°C in dilute solutions, and the speciation of aluminum and solubility of gibbsite in 0-5 molal NaCl solutions from 0 to 100°C. The solubility aluminum minerals are shown to be extremely dependent on pH, salinity and acetate concentration in solutions 1 to 2 units acid relative to the neutral pH. In neutral and basic solutions, $Al(OH)_4^-$ is the dominant aluminum species at all temperatures and salinities and the solubility in this range is only mildly affected by these variables.

7. The effect of 0.5 to 6.0 molal NaCl, 0.5 to 4.0 molal KCl, 0.5 to 5.0 moal $MgCl_2$ and $CaCl_2$, and 0.5 to 2.0 molal Na_2SO_4 and $MgSO_4$ on the D/H and $^{18}O/^{16}O$ ratios of water vapor coexisting with the brines, relative to vapor over pure water liquid of the same isotopic composition and temperature has been measured at 50, 70 and 100°C in a unique glass reaction system enabling the isolation and sampling of equilibrated water vapor at experimental conditions. The δD values of the vapor over salt solutions are uniformly larger than those over pure water, increase linearly with salinity, and are dependent on both cation and anion type. $^{18}O/^{16}O$ are opposite in sign, but are also linear with salinity and highly dependent on cation type as well as anion type.

8. The D/H and $^{18}O/^{16}O$ effects of 0.5 to 5.0 molal NaCl have been determined to 200°C in a metal pressure system similar to the glass system. The effect of 1.0 molal NaCl has been measured to 350°C in a dynamic system where vapor samples are drawn from the head space by a positive displacement pump. As at low temperature, NaCl has essentially no oxygen effect. The pure water D/H and $^{18}O/^{16}O$ liquid-vapor partitioning has been measured from 25-350°C.

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HYDROTHERMAL GEOCHEMISTRY

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Potentiometric studies of protolytic reactions in brines

The hydrogen-electrode potentiometric laboratory operated by the Geochemistry and High Temperature Aqueous Chemistry Groups in the Chemistry Division at ORNL is a unique facility which provides precise and thermodynamically-rigorous information on any homogeneous or heterogeneous aqueous reaction in which hydrogen ions are involved. The cell is capable of operation at temperatures of 0 to 295°C to pressures of about 150 bars. The cell functions by comparing the potentials of two platinum-H_2 electrodes, each of which responds thermodynamically to the half-cell reaction $H_2 = 2H^+ + 2e^-$. One electrode is immersed in a reference cup (teflon), while the other is immersed in the test solution cup (teflon). The cups are connected by a porous teflon liquid junction and solutions can be added or removed from the test compartment for titrations or sampling. Both compartments are exposed to the same hydrogen pressure, so the potential is only a function of the difference in H^+ activity and the liquid junction potential between the two cells. The latter is easily minimized by maintaining the same high concentration of supporting electrolyte (such as NaCl) in both cells. This also minimizes differences in activity coefficients and relative concentrations of H^+ can be determined. Since the cell operates under a hydrogen atmosphere, only those reactants stable or metastable (like HSO_4^-) to excess H_2 can be studied.

With this cell, we are attempting to provide the best possible information on the acid dissociation constants of important inorganic and organic acids found in geologic systems, and which influence hydrothermal fluid/rock interactions. During the reporting period, we measured the dissociation constants of bisulfate in 0.1 to 5.0 molal NaCl brines from 50 to 250°C. The results are shown in Fig. 1. With this work we have essentially completed studies of the important inorganic acids, including water and carbonic and phosphoric acids. We are now studying the important organic acids. The dissociation constants of acetic acid were measured in a BES/Chemical Sciences program. In this project, we have studied oxalic, malonic and formic acids in 0.1 to 5.0 molal NaCl to 175, 100 and 200°C, respectively (limited by the thermal stabilities of the acids) and are now studying benzoic acid. The attached reprints on formic and oxalic acid dissociation give details of measurements of this type.

The potentiometric cell is also well suited to measurements of the complexation of metal ions by the anions of weak acids. We have determined the formation constants of zinc acetate to 295° and 0.1 to 5.0 molal ionic strength, and aluminum acetate complexes to 150°C. The formation constants of $AlAc^{2+}$ in NaCl brines to 150°C are shown in Fig. 2. Finally, we have recently begun using the potentiometric (emf) cell to study the decomposition kinetics of the decarboxylation of organic acids. Fig. 3 shows results of oxalic acid decomposition measurements from conventional hydrothermal batch sampling runs and samples drawn directly from the emf cell at the same time, temperature and

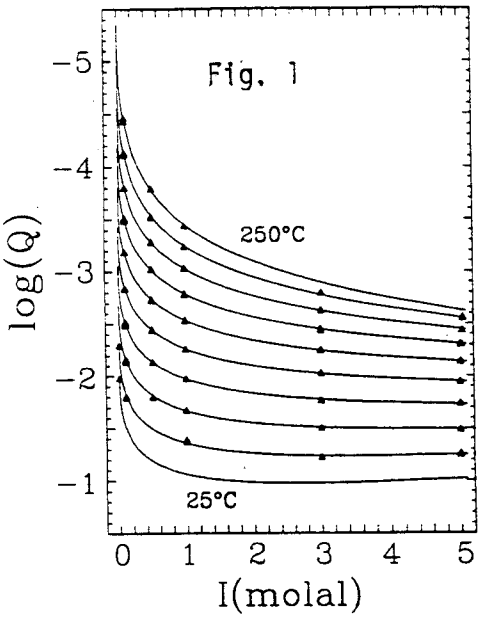
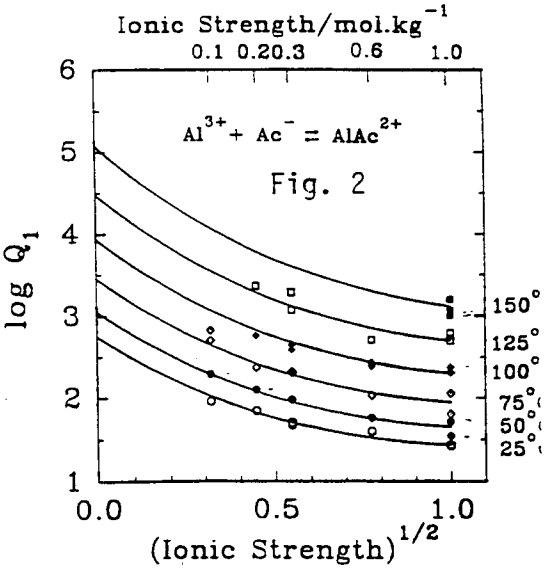
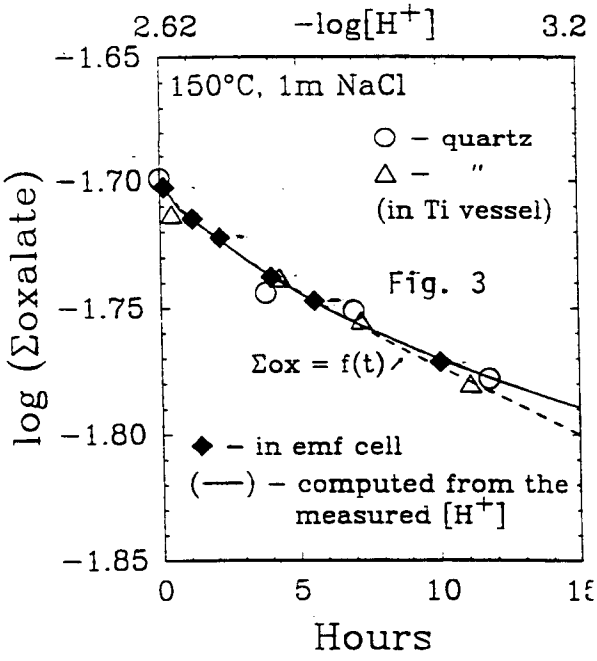


Fig. 1
log(Q)
250°C
25°C
I(molal)


Ionic Strength/mol.kg^{-1}
$Al^{3+} + Ac^- = AlAc^{2+}$
Fig. 2
log Q_1
150°
125°
100°
75°
50°
25°
(Ionic Strength)$^{1/2}$


−log[H$^+$]
150°C, 1m NaCl
○ – quartz
△ – "
(in Ti vessel)
Fig. 3
Σox = f(t)
◆ – in emf cell
(——) – computed from the measured [H$^+$]
log (Σoxalate)
Hours

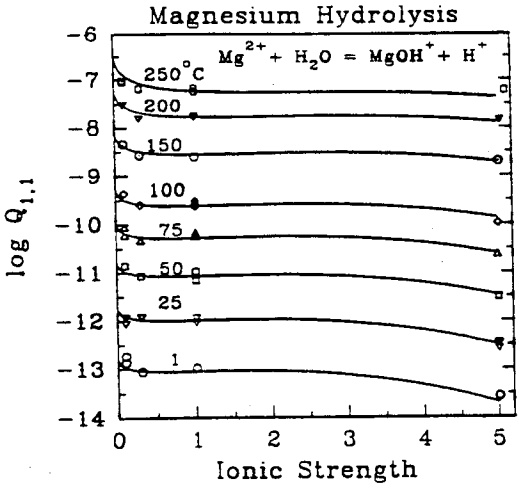
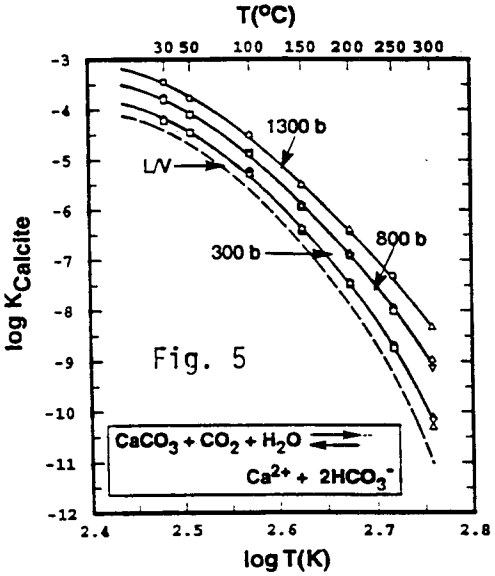
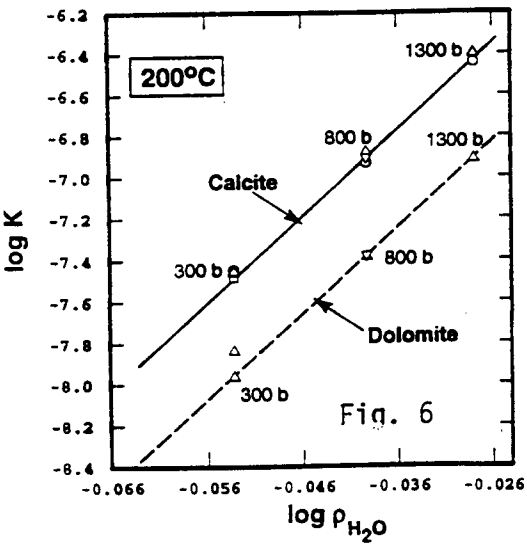

Magnesium Hydrolysis
$Mg^{2+} + H_2O = MgOH^+ + H^+$
250°C
200
150
100
75
50
25
1
log $Q_{1,1}$
Ionic Strength

Fig. 4


T(°C)
30 50 100 150 200 250 300
1300 b
L/V
800 b
300 b
log $K_{Calcite}$
Fig. 5
$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$
log T(K)


200°C
1300 b
800 b
1300 b
Calcite
300 b
800 b
Dolomite
300 b
Fig. 6
log K
log ρ_{H_2O}

solution composition. Calculated changes in total oxalate from the measured pH (coupled with mass and charge balance equations) are in exact agreement until the pH shifts to a value where the decomposition product, formic acid, changes to the formate anion, at which point the decomposition no longer involves hydrogen ions. This is an extremely powerful approach, because instantaneous rates can be computed from the pH vs time curve and the individual rates of oxalic acid, bioxalate and oxalate can be separated. We are also studying formic acid decomposition in this way.

Finally, continuing a long tradition at ORNL, we have studied the hydrolysis of Mg^{2+} to $Mg(OH)^{+}$, as shown in Fig. 4. This was made particularly difficult because of the precipitation of brucite even at magnesium concentrations in the submillimolal range. A novel experimental technique was developed for making these measurements.

Mineral dissolution, precipitation and sorption

Fluid/rock-interactions in hydrothermal systems in all crustal settings, from groundwater to sedimentary basins to geothermal systems, inevitably involve mineral dissolution, precipitation and sorption. In scanning the literature, it was immediately apparent that the data on calcite solubility was ambiguous and there was virtually no information on dolomite solubility. Since dolomitization is a major process controlling permeability development in deep fluid-flow settings, this seemed a critical need.

Fig. 5 shows our results for the solubility of calcite in relatively pure water at 30 to 300°C an 300 to 1300 bars, with reversals obtained by ramping up and down pressure at constant temperature in a gold-bag rocking autoclave. The solubility curves for dolomite look very similar and parallel the calcite solubility curves. Fig. 6 shows the solubility products for calcite and dolomite at 200°C plotted versus the density of the solvent. The linear relationships apply at all temperatures studied and the dolomite solubility product is shown to be about 0.5 log units lower than that of calcite. The data were fit to a density function and extrapolation of the calcite solubility curve to low temperature and pressure gives excellent agreement with the data of Plummer and Busenberg (1982). Our reversed solubilities for dolomite are the only ones available in the 100 to 300°C range.

Space does not permit a detailed discussion of our studies of the solubility of magnetite in acetate (pH) and magnetite/hematite (fO_2) buffers. The measured solubilities in the 250 to 1250 bar, 100 to 250°C range are entirely consistent with earlier studies of the complexation of Fe^{2+} by acetate conducted in this laboratory using our potentiometric cell. We are now using this information to extract the solubility product for $Fe_3O_4 + 2H^+ = Fe_2O_3 + Fe^{2+} + H_2O$ and the redox reaction $2Fe_3O_4 + 1/2(O_2) = 3Fe_2O_3$.

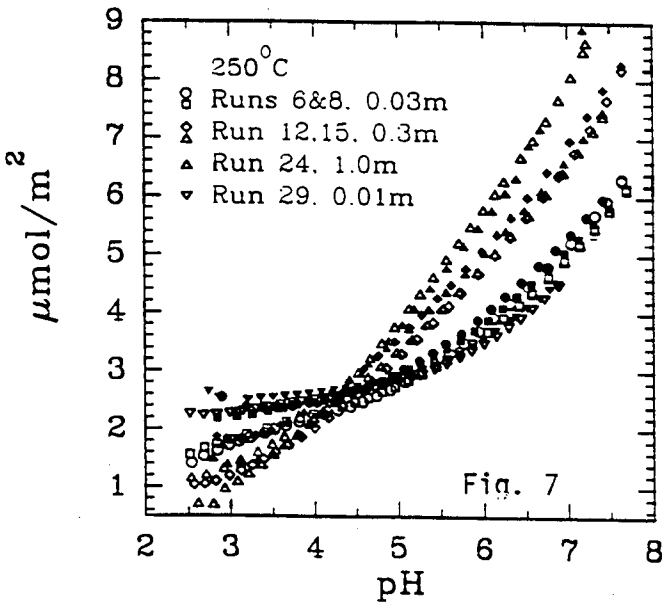
Fig.s 7 and 8 show the results of a very recent effort to use potentiometric titrations to quantify the surface properties of minerals at high temperature. Each plot shows the micromoles of H^+ adsorbed per unit area of surface as a function of pH. TiO^2 (rutile) was loaded into our potentiometric cell and equilibrated at about pH 2. The surface was then titrated with NaOH (open symbols in figures) and then back titrated with HCl (filled symbols) at constant ionic strengths of 0.01 to 1.0 molal, maintained by NaCl. Fig. 7 is a plot of the actual pH, defined here as the negative logarithm of the molal hydrogen ion

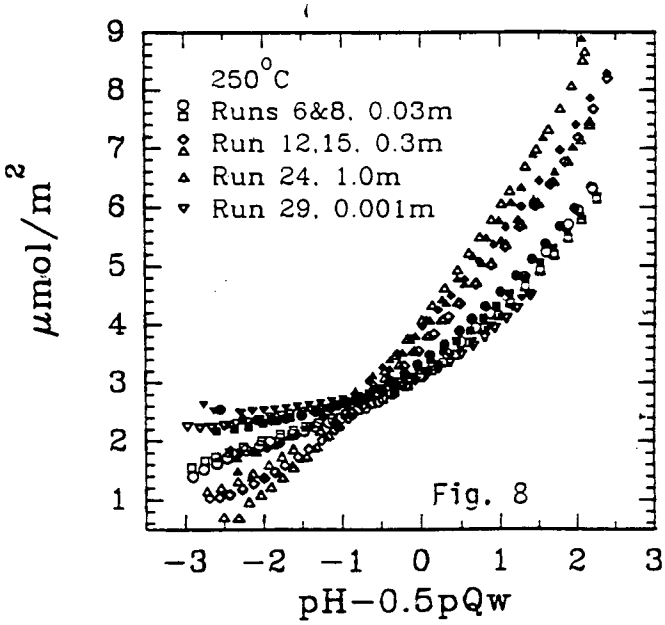
concentration (-log[H^+]) and Fig. 8 shows the same data plotted versus the difference between the measured pH and the neutral pH at each ionic strength. Both plots show a well-defined "cross-over" point, which gives the isoelectric point of the surface. This parameter controls the adsorption properties of surfaces, as well as the dissolution and precipitation rates of the bulk mineral and any sorbing or desorbing ions. Titrations of this type have been conducted from 25 to 250°C and the heats of proton adsorption agree well with calorimetric measurements. This is the first study of this type ever conducted.

Theoretical, analytical and field studies

Juske Horita is collaborating with H.D. Holland of Harvard University on studies of brine evolution in ancient evaporite deposits as a part of a long-standing effort to quantify the evolution of seawater chemistry through geologic time. The current results on the Devonian Praire Formation of Western Canada indicate substantial diagenetic interactions of the evaporites with fluids in communication with shale and sandstone units. This work is highly relevant to the modeling of sedimentary-hydrothermal systems.

Jeff Seitz is maintaining a collaboration with I-Ming Chou of the USGS and Jill Pasteris of Washington University in an effort to develop Raman spectroscopic methods for quantitative determination of gas composition and internal pressures in fluid inclusions. They have established the composition and pressure dependencies of the Raman vibrational frequencies of CH_4, N_2 and their mixtures at room temperature. This research will find broad application in the study of fluid evolution in hydrocarbon and geothermal systems.





Major Accomplishments

1. The acid dissociation constants of bisulfate (5-250°C), formic (0-200°C), oxalic (0-175°C) and malonic (0-100°C) acids have been measured in 0-5 molal NaCl brines with precisions of ±0.01 log units using our unique high temperature, hydrogen-electrode concentration cell. These studies have all been published.

2. The complexation of Zn^{2+} by acetate in 0-5 molal sodium trifluoromethane sulfonate at 50-295°C has been measured potentiometricly and published. Al^{3+} complexation by acetate in 0-1 molal NaCl brines to 150°C has been measured and submitted for publication. Measurements of the hydrolysis of Mg^{2+} to $Mg(OH)^{+}$ in 0-5 molal NaCl solutions to 250°C are completed.

3. We have succeeded, for the first time, in measuring the adsorption of H^{+} onto a mineral surface (TiO_2) in brines at elevated temperatures (250°C).

4. The solubility of calcite and dolomite in dilute aqueous solutions has been completed from 30-300°C and 300-1300 bars.

5. The solubility of magnetite in acetic acid/sodium acetate solutions with fO_2 controlled by the Fe_2O_3/Fe_3O_4 buffer has been completed at 100-250°C and 250 to 1250 bars.

6. Raman spectral parameters for pure CH_4 and N_2 and their mixtures have been determined as a function of pressure which can be used for quantitative determination of composition and pressure of gas mixtures.

7. The equilibrium constants for many hydrothermal reactions are shown to be linearly related to the density of water and extrapolatable to high pressure and temperature.

8. Major and minor element chemistry of brines in inclusions in halite from the Middle Devonian Praire Formation of western Canada indicate that the trapped waters were involved in basin-wide diagenetic processes.

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May 10, 1993

SUMMARY OF RESEARCH SUPPORTED BY DOE GRANT DE-FG03-85ER13419 (1985-1993)

1. Project Title: Advective-Diffusive/Dispersive Transport of Chemically Reacting Species in Hydrothermal Systems

Principal Investigator:

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2. Project Overview.

A. Specific Project Objectives.

1. Past.

Research in this laboratory supported by DOE in the past has been concerned primarily with 1) development of computer codes to calculate advective-dispersive/diffusional transport coupled with chemical reactions in geochemical processes at both high and low temperatures and pressures, and 2) generating values of the thermodynamic and transport properties of both organic and inorganic aqueous species in geothermal/hydrothermal systems.

2. Current.

Research being carried out at present is concerned with application of thermodynamics to organic/inorganic reactions in hydrothermal systems and hydrocarbon reservoirs to achieve a better understanding of the effects of chemical mass transfer in geochemical processes on the occurrence and evolution of energy resources in the crust of the Earth. The research currently underway is an extension and outgrowth of the past research carried out in this project.

3. Planned future work.

Future research planned for this project includes characterizing quantitatively and comprehensively the chemical interaction of crude oil with its mineralogic and aquatic environment in sedimentary basins. In addition, thermodynamic and kinetic constraints on the chemical evolution of petroleum in source rocks and hydrocarbon reservoirs will be investigated, together with the extent to which reactions at the organic-inorganic interface in sedimentary basins are mediated by hyperthermobarophilic microbes. Research plans also call for calculation of the stoichiometric and oxidative solubilities of a wide variety of hydrocarbons in oil field waters over wide ranges of pressure, temperature, and fluid composition, development of comprehensive chemical and thermodynamic models of diagenesis in hydrocarbon reservoirs, and investigation of the thermodynamic behavior of phosphorus, nitrogen, iron, and sulfur in diagenetic processes, with particular reference to the biochemical aspects of the evolution of petroleum in sedimentary basins.

B. Relation of Project to the DOE Program's Mission.

The project is directly related to the Department of Energy mission to find and use energy sources by providing fundamental research in support of national energy policy goals which is directly related to the geochemistry of geothermal/hydrothermal systems and the origin and occurrence of fossil fuel resources and their chemical interaction with minerals and interstitial waters in sedimentary basins. It also has potential application to exploration for hydrocarbon reservoirs.

C. Relation of This Project to Others Being Funded by DOE.

This project relates directly to many other energy-oriented research projects funded by DOE by providing basic research that is crucial to understanding chemical and energy transport in the upper crust of the Earth.

3. Scientific and Technical Content

A. Relation of this research to research being conducted by others in this field.

The research carried out under the auspices of DOE Grant DE-FG03 85ER13419 complements but does not duplicate related research being conducted elsewhere. The latter research includes in part that being carried out by Antonio Lasaga at Yale, Dimitri Sverjensky at Johns Hopkins, Everett Shock at Washington University, John Walther at Northwestern, Leigh Price at the USGS, Lynton Land at the University of Texas, and many others.

B. Importance of solving the problem being addressed by this research.

Application over the past decade or so of thermodynamics, kinetics, and transport theory to prediction and interpretation of the consequences of geochemical processes at elevated temperatures and pressures in the Earth has brought into question many conventional concepts concerning speciation and mineral solubilities in hydrothermal fluids, as well as the origin, migration, and occurrence of hydrocarbons and the extent to which they interact chemically with their surroundings in sedimentary basins. For example, new insights suggest that world oil reserves have been grossly underestimated and that understanding the origin and migration of petroleum, as well as effective use of compositional data to enhance exploration for, and development of hydrocarbon resources requires comprehensive and quantitative investigation of the chemical interaction of organic solids, liquids, and gases with aqueous solutions and minerals in sedimentary basins. Because this is the overall objective of this project, the project is of fundamental importance to full realization of the energy potential of fossil fuels in the crust of the Earth.

C. Schedule of major research activities.

During the early years of this project, research was focused on development of comprehensive mathematical models of advective-diffusive/dispersive transport coupled to chemical reactions in geothermal/hydrothermal systems. Massive computer codes were generated to accomplish this objective, but many of the requisite parameters were not available to apply the codes to realistic description of chemical mass transfer in geochemical processes, especially at elevated temperatures and pressures. Accordingly, equations of state were developed to calculate the thermodynamic and transport properties of aqueous species and the various kinetic parameters required to describe their chemical interaction with minerals at depth in the Earth. More recently, research efforts have been concentrated on calculation of speciation and mineral solubilities in hydrothermal solutions and the thermodynamic properties of organic solids, liquids, and gases at elevated temperatures and pressures.

The original Helgeson-Kirkham-Flowers (HKF) equations of state for calculating the standard partial molal thermodynamic properties of aqueous species were revised during the course of this project to be consistent with temperature/pressure-dependent effective electrostatic radii of aqueous ions. New equations-of-state correlations were developed which can be used to predict thermodynamic properties of aqueous species for which little or no experimental data are available. These equations of state and correlations were incorporated in a computer code named SUPCRT92, which can be used to calculate accurate values of the thermodynamic properties of reactions among a wide variety of minerals, gases, and aqueous species at high temperatures and pressures, including both organic and inorganic ions, complexes, and neutral molecules. The code was developed with partial support from DOE, and it has since been distributed worldwide in response to requests from nearly 300 different laboratories.

Calculations carried out under the auspices of DOE Grant DE-FG03-85ER13419 over the past eight years include dissociation constants of 1:1 alkali ion pairs, metal ion complexes, and polynuclear clusters in hydrothermal solutions, as well as tracer diffusion coefficients of both organic and inorganic aqueous species and limiting equivalent conductances, Stokes' law radii, residual friction coefficients, and Walden products for a large number of ionic species as a function of temperature and pressure. Other research activities include calculation of activity coefficients for charged and neutral aqueous species at elevated pressures and temperatures, development and application of improved computational codes to describe organic/inorganic interaction and mass transfer in hydrocarbon reservoirs, calculation of the solubilities of minerals in hydrothermal solutions, and generation of bulk composition-pH-log $f_{O_{2(g)}}$ diagrams for minerals and mineral assemblages to better interpret stability relations in diagenetic systems as a function of temperature, pressure, composition, reaction progress, solution pH, and the fugacity of oxygen ($f_{O_{2(g)}}$) in the system.

During the evolution of this project over time, sufficient progress has been made in characterizing the thermodynamic and transport properties of both organic and inorganic aqueous species as well as organic solids, liquids, and gases at elevated temperatures and pressures that comprehensive thermodynamic analysis of energy resources in the crust of the Earth can now be made over wide ranges of temperature, pressure, and composition. Research plans call for expansion of the project in the future to permit such analyses of the role of water and oxidation/reduction reactions in source rock generation and maturation of hydrocarbons, thermodynamic and chemical constraints on the transport and migration of oil in the presence of water, and the chemical interaction of oil field waters with organic species and minerals in young dynamic basins. Related research will be concerned with the relative stabilities of biomolecules required for the survival of hyperthermobarophilic microbes at depth in the Earth. Experimental data suggest that such microbes may be thriving at the oil-water interface in hydrocarbon reservoirs at temperatures and depths well in excess of those generally thought to be hospitable to microbial life.

D. Scientific and technical issues currently being addressed and their significance.

The major scientific and technical issues of concern in this project at the present time are: 1) how reactive are organic molecules at elevated temperatures and pressures in sedimentary basins, 2) how prevalent are metastable equilibrium states involving these molecules and the minerals and waters in source rocks and reservoirs, 3) what is the role of oxygen fugacity relative to temperature and pressure in breaking down organic matter to hydrocarbons and the maturation of petroleum in source rocks, 4) what are the congruent and incongruent solubilities of detrital minerals in oil field waters and what role do organic species in petroleum play at the oil-water interface in determining these solubilities and generating secondary porosity resulting from mineral dissolution, and 5) what is the role of water and hyperthermobarophilic microbes in the generation and maturation of petroleum at depths in excess of ~3 km?

E. Experimental and theoretical approach taken, techniques used, and resources applied.

So far, the approach taken in this project has been entirely theoretical, consisting of the application of thermodynamics, chemical kinetics, transport theory, and other aspects of theoretical geochemistry to analysis of experimental data reported in the literature and interpretation of phase relations in hydrothermally altered rocks in metamorphic and diagenetic systems. The techniques used and resources applied are almost entirely computer techniques and human resources. However, future plans call for development of experimental capabilities to investigate the reactivities and relative stabilities of organic and biochemical molecules and microbes under conditions prevailing in hydrocarbon reservoirs. Conventional pyrolysis experiments are of little use in this regard. It thus appears that experimental and analytical techniques and resources will be required for the project in the future.

4. Project Output

A. Major recent research accomplishments with supporting data and their significance.

Recent accomplishments in research supported by DOE in this laboratory are concerned with the chemical interaction of petroleum, oil field waters, and minerals at the oil-water interface in hydrocarbon reservoirs. Although the presence of carboxylic acids and carboxylate anions in oil field waters is commonly attributed to the thermal maturation of kerogen or bacterial degradation of hydrocarbons during water-washing of petroleum in relatively shallow reservoirs, they may have also been produced in deeper reservoirs by the hydrolysis of hydrocarbons in petroleum at the oil-water interface. To test this hypothesis, calculations were carried out to determine the distribution of species with the minimum Gibbs free energy in overpressured oil field waters in the Texas Gulf Coast assuming metastable equilibrium among calcite, albite, and a representative spectrum of organic and inorganic aqueous species at reservoir temperatures and pressures. The cohort of waters chosen for this purpose was restricted to include only those for which analyses reported in the literature list separately analytical concentrations of both organic and inorganic carbon. These values were specified in the Gibbs free energy minimization calculations to constrain the fugacity of oxygen ($f_{O_{2(g)}}$). This constraint is predicated on the hypothesis that the oxidation of carboxylic acids to CO_2 in oil field waters is rapid in the context of geologic time, but slow in terms of the time span of laboratory studies. The calculations resulted in credible solution pHs and activities of aqueous CO_2 ($a_{CO_{2(aq)}}$). It can be seen in Fig. 1 below that the values of $\log f_{O_{2(g)}}$ generated by the calculations exhibit a remarkably smooth distribution with temperature which is similar to, and within the range of those characteristic of common mineral assemblages. Similar variation with temperature is exhibited in Fig. 2 below by values of $\log f_{O_{2(g)}}$ resulting from calculation of the distribution of species with the minimum Gibbs free energy in oil field waters recovered from the San Joaquin basin of southern California.

The observations summarized in the preceding paragraph strongly support the hypothesis that homogeneous equilibrium obtains among carboxylate and carbonate species in oil field waters and that the fugacities of oxygen consistent with this metastable equilibrium state are indicative of those obtaining in hydrocarbon reservoirs at depth. To determine the extent to which these species may also be in metastable equilibrium with hydrocarbon species in petroleum at the oil-water interface, representative values of the computed fugacities of oxygen in hydrocarbon reservoirs in the Texas Gulf Coast were used together with corresponding values of $a_{CO_{2(aq)}}$ in the waters to calculate equilibrium activities of various hydrocarbon species in crude oil. The calculations resulted in reasonable activities of *n*-alkanes with carbon numbers $\gtrsim$ 6–15, depending on the activity of aqueous CO_2. However, it appears that *n*-alkanes with lower carbon numbers in crude oil cannot achieve heterogeneous metastable equilibrium with oxidized carbon-bearing species in the crust of the Earth. The calculations also indicate that Ca^{2+}, H^+, CO_2, CH_3COOH, CH_3COO^-, and other aqueous species in oil field waters may be in metastable equilibrium at the oil-water interface with hydrocarbons other than the light paraffins in crude oil, as well as with calcite and other minerals in hydrocarbon reservoirs. If this is indeed the case, the compositions of formation waters can be used together with Gibbs free energy minimization calculations to guide sequential exploration drilling for hydrocarbon accumulations in sedimentary basins. Both thermodynamic and compositional considerations suggest that the fugacity of oxygen in calcite-bearing reservoirs may be controlled at the oil-water interface by metastable equilibrium states among the heavier hydrocarbons in crude oil and/or calcite and the oxidized carbon-bearing species in the aqueous phase. Irreversible reaction of the light paraffins in petroleum with H_2O at the oil-water interface to form lighter paraffins and $CO_{2(aq)}$, $CH_3COOH_{(aq)}$, and other oxidized carbon-bearing aqueous species is strongly favored by the large chemical affinities of the reactions. Because these irreversible hydrolytic disproportionation reactions are both exergonic and endothermic, they may be mediated at high temperatures and pressures by hyperthermobarophilic archea or bacteria. However, the extent to which this occurs at the oil-water interface in any given reservoir may depend on whether or not methane produced by the reactions can escape from the system. Although analytical data reported in the literature indicate that maturation of crude oil does not occur to an appreciable degree in static hydrocarbon reservoirs, irreversible hydrolytic disproportionation of the light paraffins in petroleum favors maturation of crude oil in flow channels and reservoirs in young dynamic basins in which fluid

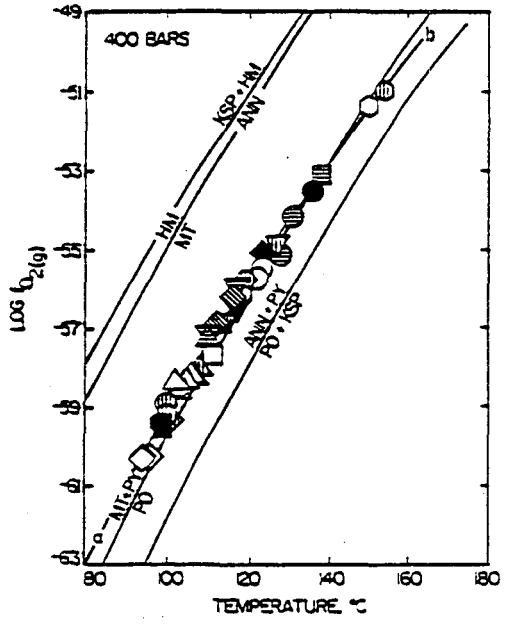

Fig. 1. Log $f_{O_{2(g)}}$ as a function of temperature at 400 bars computed from the distribution of aqueous species with the lowest Gibbs free energy in oil field waters in the Houston-Galveston and Corpus Christi areas of the Texas Gulf Coast represented by the symbols depicted above assuming metastable equilibrium among calcite, albite, and the organic and inorganic aqueous species in the waters after specifying separately the concentrations of organic and inorganic carbon reported as CH_3COO^- and HCO_3^-, respectively, by Kharaka et al. (1977, Proceedings, *3rd Geopressures-Geothermal Energy Conference*, GI 121-155). The curves annotated with mineral abbreviations (see caption of Fig. 3 below for abbreviations other than HM, which refers to hematite) were generated from statements of the law of mass action assuming unit activities of H_2O and the components of the minerals shown in the reactions. Curve *ab* represents a graphic fit of the distribution of the symbols.

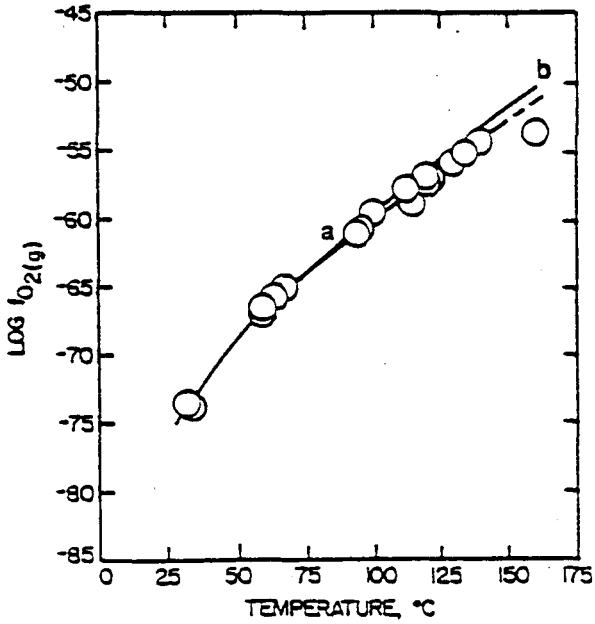

Fig. 2. Log $f_{O_{2(g)}}$ as a function of temperature at 400 bars obtained by calculating the distribution of species with the lowest Gibbs free energy in oil field waters in the San Joaquin basin represented by the symbols shown above assuming metastable equilibrium among calcite, albite, and the organic and inorganic aqueous species in the waters after specifying separately the analytical concentrations of organic and inorganic carbon reported by Fisher and Boles (1990, *Chem. Geol.* 82, 83-101). Curve *ab* corresponds to the curve labeled *ab* in Fig. 1.

flow is extensive and oil, water, and gas are in pervasive contact. It appears that irreversible production of carbonic and carboxylic acids during the hydrolytic disproportionation of the light paraffins in petroleum at the oil-water interface may drive much of the diagenetic process in such basins by lowering the pH of the oil field waters. At near-neutral pHs, the reactions favor precipitation of carbonates, but at lower pHs they favor carbonate dissolution, albitization of plagioclase, illitization of smectite, and other diagenetic reactions. These observations have far-reaching implications with respect to the development and fate of secondary porosity in hydrocarbon reservoirs, as do the solubility calculations summarized in the following paragraph.

Aqueous solubilities in oil field waters of nonane ($C_9H_{20(l)}$) in crude oil represented by reduced activities of $C_9H_{20(l)}$ have been calculated as a function of oxygen fugacity ($f_{O_{2(g)}}$) at various temperatures and 400 bars. The results of the calculations were used to generate log η_C – log $f_{O_{2(g)}}$ phase diagrams, where η_C represents the number of moles of carbon in the system (kg H_2O)$^{-1}$. One such diagram is depicted in Fig. 3, where the solubilities of carbonates and (as an example) the oxidative solubility in idealized oil field waters of nonane in crude oil are portrayed as a function of log $f_{O_{2(g)}}$ at 118°C and 400 bars. It can be seen in this figure that the oxidative solubility in the aqueous phase of nonane in crude oil at 118°C and 400 bars increases dramatically with increasing log $f_{O_{2(g)}}$ above ~ –59 in response to the oxidation of $C_9H_{20(l)}$ in petroleum to form aqueous CO_2, *n*-carboxylic acids, aromatics, and other organic aqueous species at the oil-water interface. It can be deduced from Fig. 3

that the calculations yield results consistent with the composition of oil field waters recovered from the Upper Weiting formation of the Texas Gulf Coast, as well as with metastable equilibrium among nonane in crude oil and ankerite, calcite, and dolomite. As in the case of the hydrolytic disproportionation of hydrocarbons, oxidative dissolution of crude oil at the oil-water interface in hydrocarbon reservoirs may lead either to precipitation or dissolution of carbonate minerals, depending on the pH of the aqueous phase. Phase diagrams like that in Fig. 3 afford a convenient means to assess the consequences of metastable equilibrium states in hydrocarbon reservoirs.

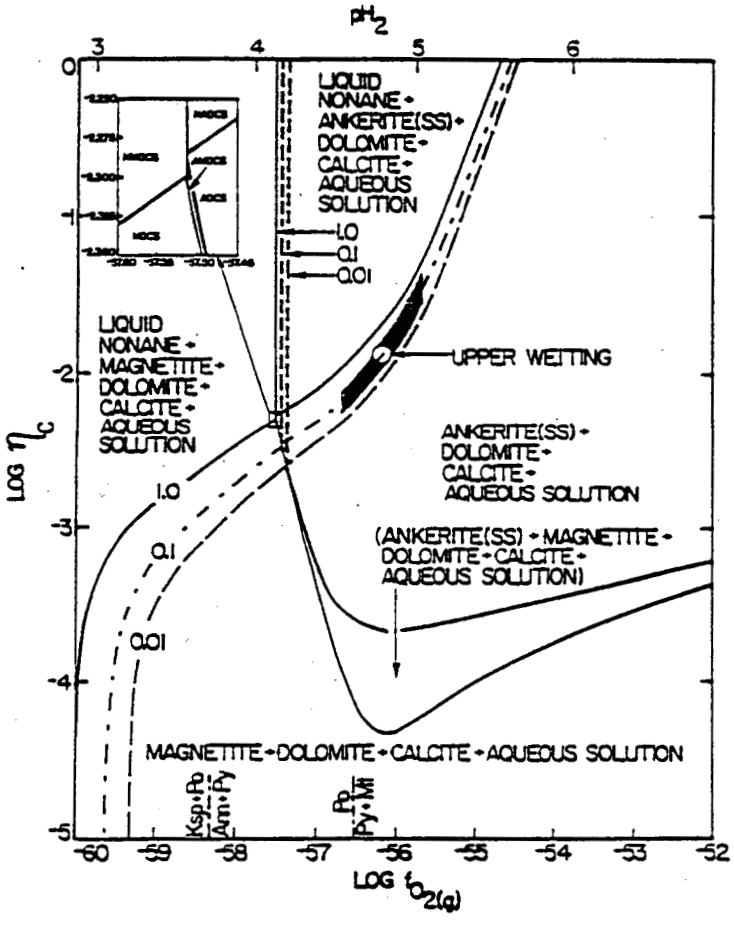

Figure 3. Log ηC – log $fO_{2(g)}$ diagram for part of the system CaO-MgO-FeO-NaCl-HCl-CO_2-O_2-H_2O in which the aqueous phase contains 1.15 m_{NaCl}, 0.05 m_{CaCl_2}, 0.009 m_{MgCl_2}, and 0.0002 m_{FeCl_2} in the presence of calcite at 118°C and 400 bars. This water composition is a proxy for the analysis reported by Kharaka et al. (1977, see caption of Fig. 1) of the Upper Weiting formation water recovered from the Anglo No. 3 well in the Texas Gulf Coast, which is represented by the symbol labeled Upper Weiting. The numbers on the solid, dot-dashed, and dashed solubility curves for nonane in crude oil refer to alternate activities of $C_9H_{20(l)}$. The mineral abbreviations for the log $fO_{2(g)}$ buffers shown in the lower part of the diagrams represent K-feldspar (KSP), annite (ANN), pyrite (PY), pyrrhotite (PO), and magnetite (MT). The shaded area depicted above represents the range of log $fO_{2(g)}$ in which hydrocarbons other than the light paraffins in crude oil can be in metastable equilibrium with CO_2 and other oxidized carbon-bearing species in the coexisting aqueous phase. The abbreviations in the enlargement graph in the upper left corner of the diagram stand for: nonane in crude oil + magnetite + dolomite + calcite + aqueous solution (NMDCS), nonane in crude oil + ankerite solid solution + dolomite + calcite + aqueous solution (NADCS), ankerite solid solution + magnetite + dolomite + calcite + aqueous solution (AMDCS), magnetite + dolomite + calcite + aqueous solution (MDCS), and ankerite solid solution + dolomite + calcite + aqueous solution (ADCS), respectively. The scale at the top of the graph refers to the negative logarithm of the activity of aqueous H_2.

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Missing Abstract

A.C. Lasaga
Reactive fluid flow models and applications to diagenesis, mineral deposits and crustal rocks

Mechano-Chemical Self-Organization and Nonlinear Dynamics in Sedimentary Basins

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ABSTRACT

Phenomena central to basin diagenesis arise out of the strong coupling of processes and cannot be understood via the analysis of the individual processes. The most dramatic of these effects emerge when feedback loops are set up in the reaction-transport-mechanical (RTM) process network. The objective of this project is to develop quantitative RTM models and simulate them on the computer to delineate the feedbacks and consequent phenomena that may exist in the deeper parts of a sedimentary basin.

Phenomena being analyzed include: 1) development of stylolites and diagenetic banding via pressure solution and their role as pressure seals and fluid conduits; 2) episodic, oscillatory fluid release from overpressured regions through a cycle of fracture genesis and healing coupled to fluid transport and pressurizing mechanisms; and 3) self-arresting and -promoting flows of fluids that react with (and change the permeability of) the rocks they traverse. Our analysis yields the conditions (basin thermal, sedimentary and tectonic history) favorable for these phenomena and their present-day implications (i.e., distribution of texture, mineralogy, and fluid pressure, composition and temperature in the basin).

Techniques used in the analysis of the RTM models include adaptive finite elements, homogenization theory and parallel computation. Without such techniques the simulation of fine scale structure and overall basin diagenesis needed to capture these phenomena would not be possible.

Applications to exploration, resource assessment and production follow from implications for petroleum generation, migration and trapping. Our RTM models and simulators serve to integrate the findings of other DOE-supported researchers working on individual (i.e., uncoupled) processes.

I. PROJECT CONCEPT

A sedimentary basin evolves via a network of reaction, transport and mechanical (RTM) processes. As these processes may be strongly coupled, many diagenesis phenomena can only be understood in terms of a number of simultaneous RTM processes and not an individual process.

Since the 1970s the principal investigator and many other physicists and chemists have been developing and using dynamical systems and bifurcation and multiple scale analysis to discover and analyze self-organization and other nonlinear phenomena in strongly coupled RTM systems (see the volumes by Nicolis and Prigogine, 1977; Field and Burger, 1985; Ortoleva, 1992, 1993a). The objective of this project is to use this very powerful approach to solve key problems in deep basin diagenesis.

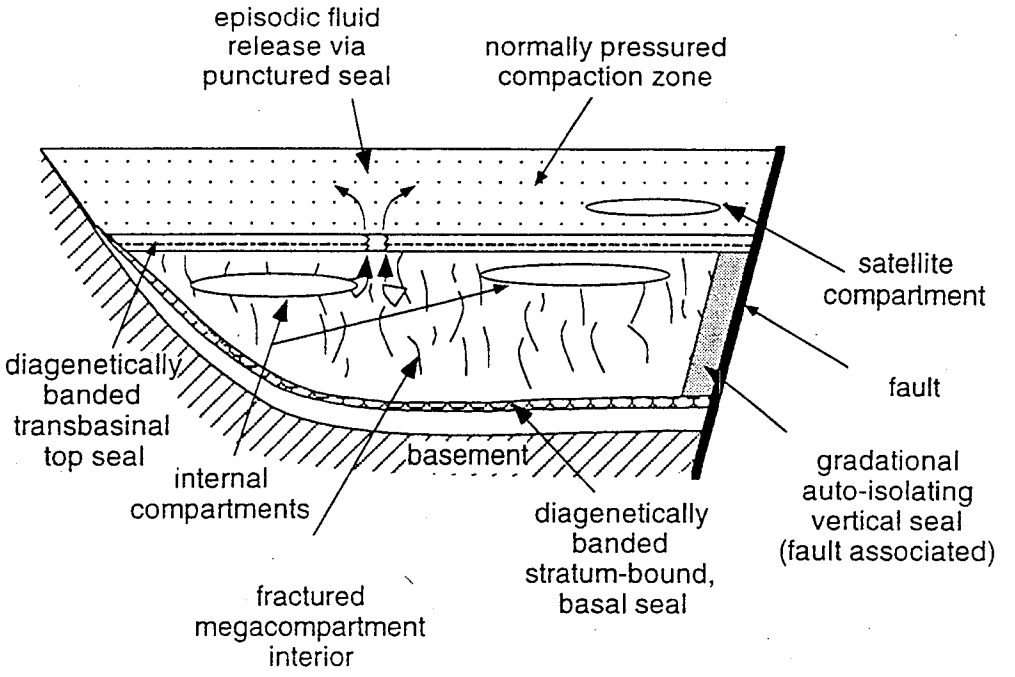


Fig. 1 Schematic view of a basin-scale overpressured region defined by a banded trans-basinal top seal, a stratum localized bottom seal, a fault-associated auto-localizing side seal and a fractured interior. A rupture in the top seal with concomitant episodic fluid release is also indicated.

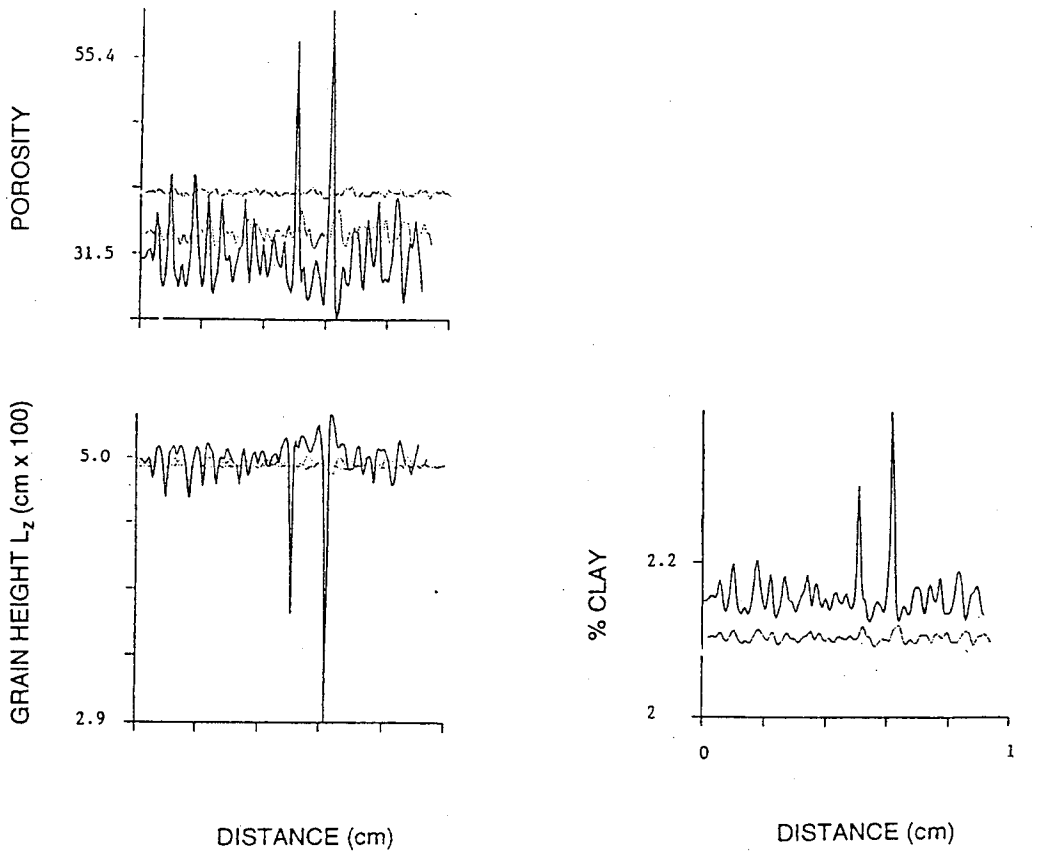


Fig. 2 Diagenetic bedding may self-organize in argillaceous limestone as observed by Ricken (1986) and here predicted by our RTM model. Evolution of profiles of porosity, grain height and clay volume fraction illustrate amplification of small nonuniformities into a marl/limestone alternation banding. The initially small amplitude variations are amplified at their final time (8,142 years).

Self-organization is the process by which a system develops undulatory patterns of descriptive variables without the imposition of these patterns in the initial distribution or at the boundaries of the system. Three factors which have been found to be required for self-organization are (Nicolis and Prigogine, 1977; Field and Burger, 1985):

* feedback in the network of RTM processes,
* quadratic or other nonlinear dependence of the rates of processes on descriptive variables (concentration, pressure, stress); and
* displacement of the system sufficiently far-from equilibrium.

A variety of self-organization and other nonlinear phenomena in geochemical systems have been identified (Ortoleva et al., 1987a, 1990; Ortoleva, 1993a). Our particular focus here is self-organization and other nonlinear phenomena in a sedimentary basin (Ortoleva, 1993a-d).

A partial list of the nonlinear phenomena in sedimentary basins that have been identified to date are (Dewers and Ortoleva, 1988; Ortoleva, 1993a-d):

* Oscillatory intra-crystal zoning in calcite (Ortoleva, 1990, 1993a).
* Repetitive episodic fluid release from depth (Ghaith et al., 1990; Dewers and Ortoleva, 1993b; Ortoleva and Al-Shaieb, 1993).
* Diagenetically differentiated marl/limestone bedding (Dewers and Ortoleva, 1993a; Ortoleva et al., 1993).
* Differentiated compaction/cementation bands in sandstones (Dewers and Ortoleva, 1990c-e, 1992).
* Stylolite arrays (Dewers and Ortoleva, 1990c-e, 1992, 1993a; Ortoleva et al., 1993).
* Reaction front fingering (Chadam et al., 1986, 1988, 1990; Chen and Ortoleva, 1990a,b, 1992, 1993; Chen et al., 1993).
* Oscillatory and fingered petroleum migration (Chen et al., 1990; Park et al., 1990; Ghaith et al., 1990).

In this project we will focus on three nonlinear phenomena:

* Diagenetic bedding, stylolites and related phenomena and their implications for basin scale, hydrology and mechanics;
* Episodic fluid release from overpressured zones; and
* Self-arresting flows occurring through a feedback involving pressure dependent reactions.

These studies will add to our developing picture (see Fig. 1) of a sedimentary basin as a system rich in self-organization and other nonlinear phenomena.

II. GENERAL GOALS

1. Identify self-organization and other nonlinear phenomena occurring during diagenesis.
2. Determine key RTM processes that couple to yield these phenomena.
3. Set forth descriptive variables and rate laws capturing the RTM processes.
4. Write general RTM simulators accounting for 2 and 3 using most up-to-date numerical methods and thermal, kinetic and transport parameter data banks.
5. Delineate characteristics presently observable (i.e., spatial, distributions of petrologic, pore fluid chemical, pressure and temperature variables) and identify precise sedimentological, thermal and tectonic histories favoring the phenomena.
6. Underscore potential implications for petroleum and mineral exploration and production.

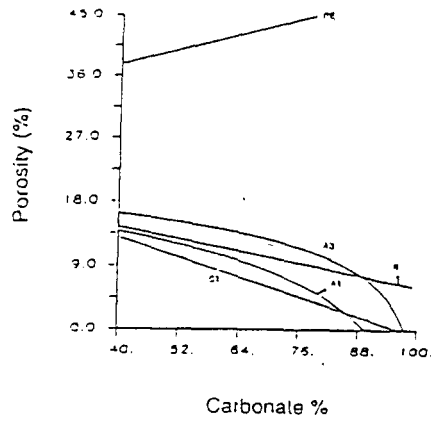
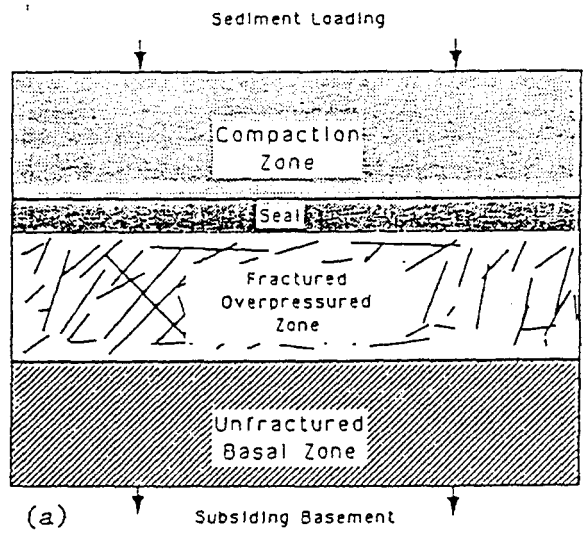


Fig. 3 *Correlation plot for examples of marl/limestone alternations from Ricken (1986) showing relations between porosity and compaction. Labels refer to individual localities; the upper curve is for a young system in which no appreciable diagenesis had occurred whereas after diagenesis the slope of the correlation becomes negative as a feature well captured by our model. Clay content increases from study areas A2, A1, G1, to R.*



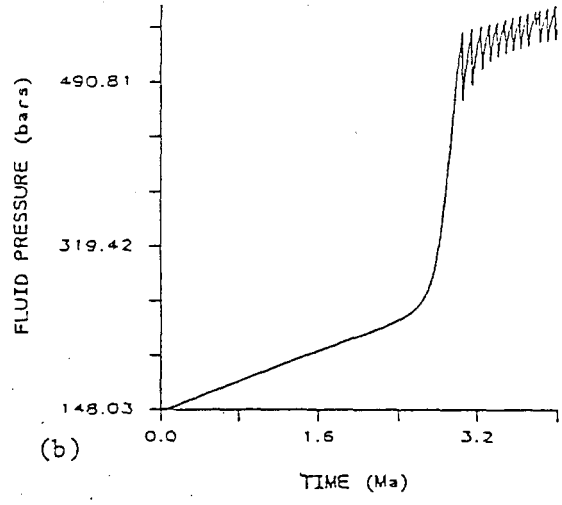


Fig. 4a *Configuration of a one-dimensional burial diagenesis model showing sediment infilling at the top, region of pressure solution-mediated compaction under hydrostatic fluid pressure, "seal" region where overall permeability (matrix plus fracture contributions) is a minimum and hydrofractured overpressured zone. Deeper, fracturing could be repressed because of increased lateral stress giving an effective lower seal.*

Fig. 4b *Numerical simulation of the RTM model of the system in Fig. 4a. Shown is the temporal evolution of the piezometric pressure at the sediment-basement interface. See Dewers and Ortoleva (1993a) for further details.*

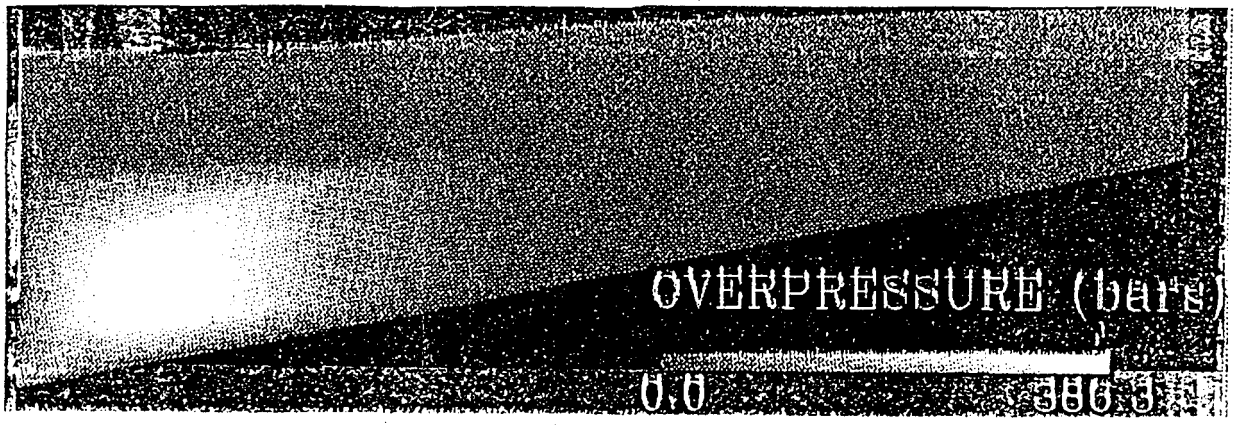


Fig. 5 200 km wide rift basin after 40 my of simulation. The maximum depth below sea level is 7.3 km. Shown is predicted fluid overpressure; hydrofracturing (not shown) resides within the overpressured domain (from Sonnenthal et al., 1993).

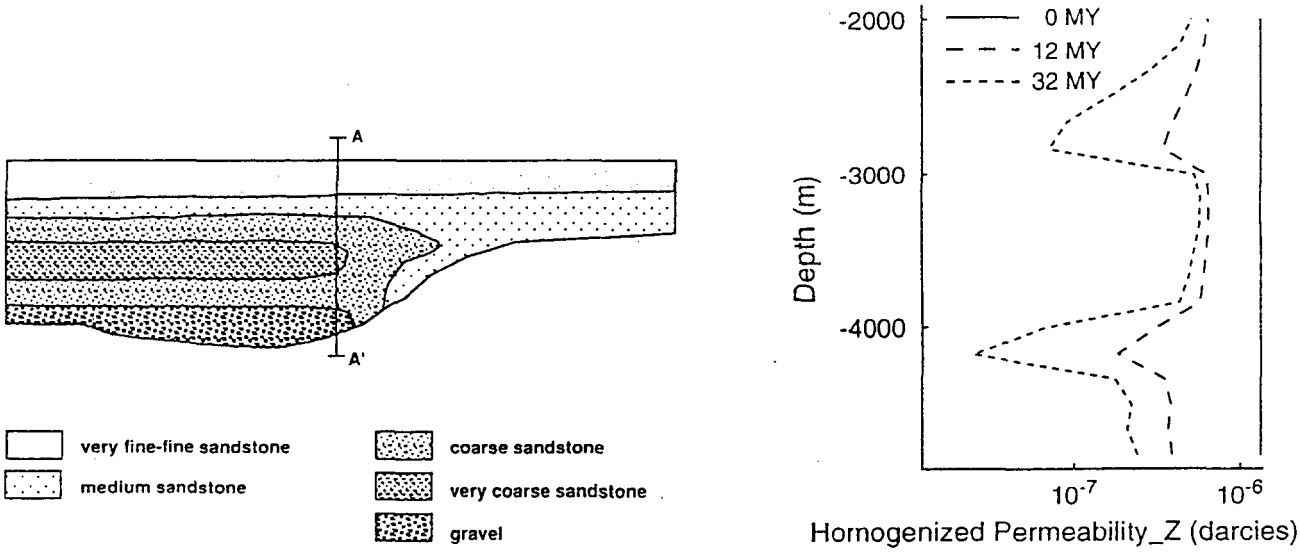


Fig. 6 Development of seals within fine grain beds. (a) Initial assumed sedimentology of the basin. (b) Graph of model predicted averaged (homogenized) vertical permeability along transect AA' after 32 my of diagenesis. Simulation carried out using the homogenization approach. Upper and lower seals are similar to those observed bounding a basin-wide overpressured domain in the Anadarko basin (Tigert and Al-Shaieb, 1990; Al-Shaieb et al., 1993).

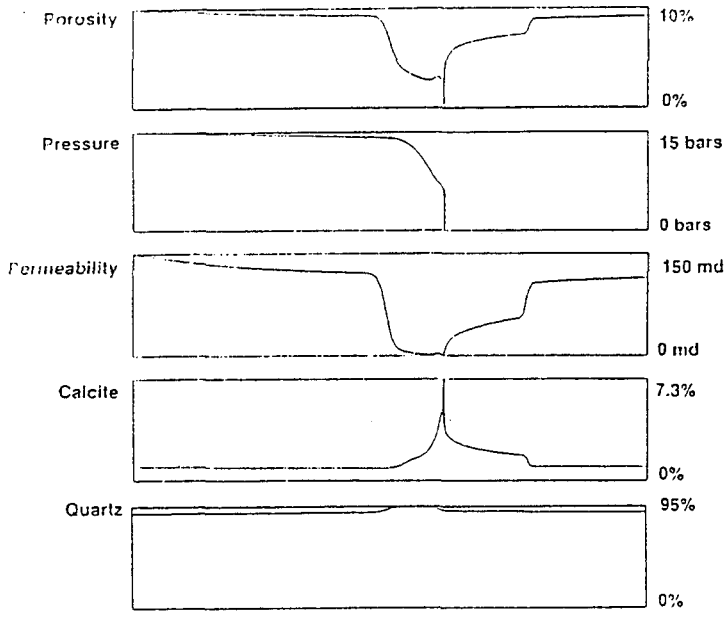


Fig. 7

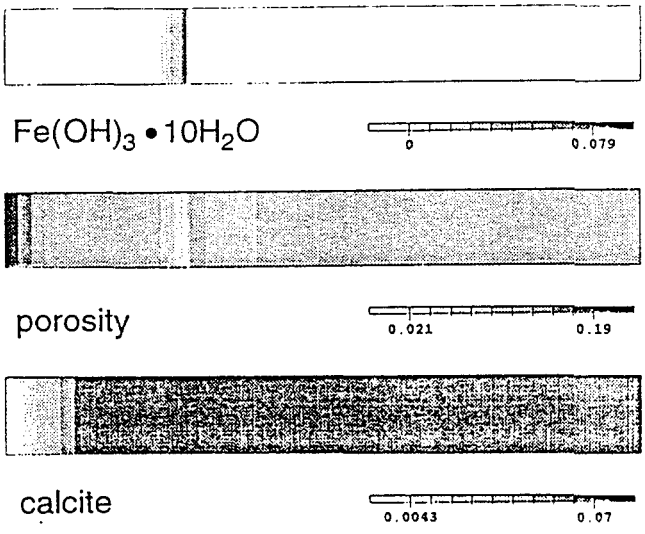


Fig. 8

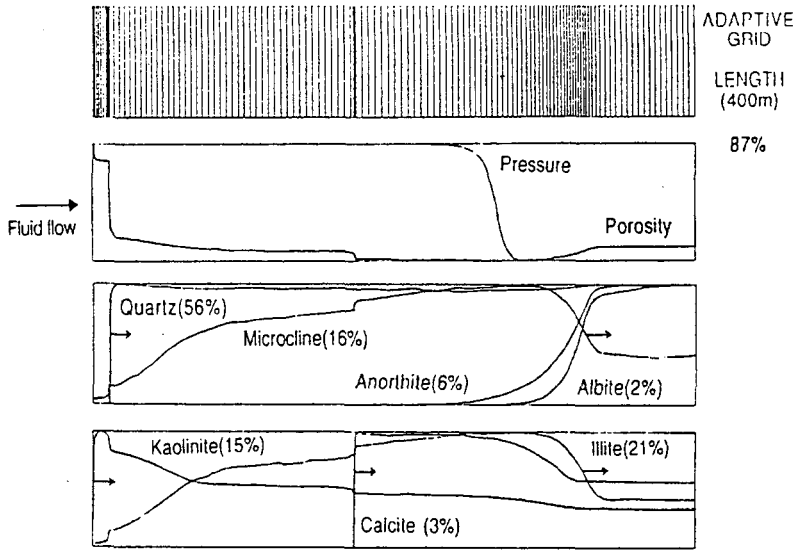


Fig. 9

Fig. 7 Calcite precipitation is focused to a narrow region through a positive feedback arising from the pressure-dependence of the calcite and related aqueous phase reactions. The flow is from the left, the simulation was for 3,780 years and the domain is 150 meters in length.

Fig. 8 A simulation of near borehole acidizing. Half strength mud acid is injected at the left for about 0.5 hours. The simulation is carried out on a 25x3 cm domain at 70°C. The porosity at the left end increased due to the dissolution of calcite and other minerals. The precipitation of Fe^{3+} gel 7 cm away from the borehole causes porosity and permeability to decrease below the original value. Excessive near-borehole dissolution and downstream gel precipitation caused formation damage that could be avoided using our infiltration code to design better mud acid composition.

Fig. 9 Simulation of the infiltration-driven diagenesis of an arkose showing resulting rock volume fractions and adapted grid after 400,000 years. Maximum amounts observed are given in parentheses. The initial rock composition was fixed to be 55% quartz, 11% microcline, 7% anorthite, 6% kaolinite, 2% calcite, 1% illite, 1% albite, and 17% porosity. Maximum amounts observed are given in parentheses.

III. WORK COMPLETED AND PLANNED ON SPECIFIC SELF-ORGANIZATION PHENOMENA

The picture emerging after the first two years of this project is that the basin is rich with self-organization and other nonlinear phenomena. Consider the schematic cross-section of Fig. 1. In Figs. 2-9 and their captions we present some of our modeling results of this project that led us to this picture. Specific phenomena to be analyzed and the associated challenges are as follows.

A. Diagenetic Bedding and Stylolites: Origins and Basin-Scale Implications

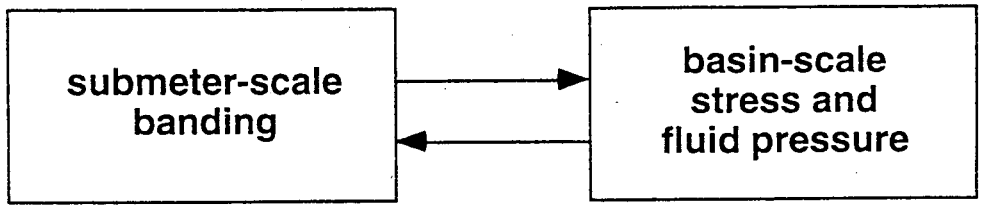
1. Work completed

A variety of millimeter- to meter-scale roughly planar features appear to have either differentiated out of uniform sedimentary rock or result from some intensification of a preexisting sedimentary feature. These include (see Ortoleva, 1993a-d and Ortoleva and Al-Shaieb, 1993 for references):

* banded calcite cements in sandstones;
* roughly evenly spaced arrays of stylolites in limestones and sandstones;
* diagenetically differentiated bedding in marl/limestone sequences;
* layers of enhanced intergranular pressure solution in sandstones;
* mica laminations in very fine grained sandstones;
* spaced cleavage and stylolites in a variety of rocks;
* fine-scale diagenetically differentiated lamination in shales and chalk; and
* banded pressure seals in a sedimentary basin.

We have already been successful in explaining most of these observed phenomena using our RTM models (see Dewers and Ortoleva, 1990c, 1993b; Ortoleva and Al-Shaieb, 1993; and Ortoleva, 1993a-d for references). A typical result is seen in Fig. 2. The switch of the slope of the correlation plot of porosity and calcite mode from its positive (sedimentary) situation to the negative correlation after diagenesis (Fig. 3) are the result of mechano-chemical feedback. The observations of Ricken (1986) shown in Fig. 3 and the predictions of our model are in good agreement (Dewers and Ortoleva, 1993a).

The bands may develop very low permeability through precipitation of locally derived cements. Thus banded regions may serve as barriers to flow and thereby affect the basin scale distribution of fluid pressure as observed in the Anadarko basin (Tigert and Al-Shaieb, 1990; Al-Shaieb et al., 1993; Shepherd et al., 1993). As this pressure affects grain stress and thereby the pressure solution dynamic, we see that there is a multiple scale nature of the basin evolution:



Clearly, capturing centimeter-scale banding in a basin scale system is unfeasible by straightforward methods. We address this modeling challenge to capture this type of tightly coupled two-scale dynamic via homogenization theory briefly in Sect. V.

2. Work in progress

In the remainder of this project we shall further develop our mechano-chemical model to enable us to capture multi-mineral phenomena such as banded silica cements and stylolites in arkose sandstone. We shall also investigate the resulting centimeter-

and basin-scale distribution of texture. This may give us new constraints on interpreting basin histories as the banding phenomena depend sensitively on sedimentary, thermal and tectonic history. Our two-dimensional result is shown in Fig. 6 and our simplified homogenization calculations in three dimensions have also already been done.

B. Oscillatory Fluid Release

1. Work completed

Nonlinear and linear oscillations are fundamentally different. In the latter case, the amplitude is fixed by the initial state. For nonlinear oscillations in far-from-equilibrium systems the amplitude depends on the rate and other parameters in the RTM phenomenological laws and not on initial data.

We have illustrated periodic nonlinear oscillations (e.g., a limit cycle) in a basin experiencing sediment loading, poroelasticity and force balance, pressure solution, and thermal fluid expansion. The general picture that is emerging is seen in Fig. 4a and a simulation is seen in Fig. 4b (Dewers and Ortoleva, 1993b). We have demonstrated in this and similar simulations the following:

a. A dynamic hydrofracture front that rises up the incoming sediment.
b. The front can become unstable beyond a critical sediment loading rate (or as other sedimentary, thermal or tectonic factors change);
c. The periodic oscillation takes place even if the sediment loading rate (and other parameters) are time-independent.
d. A hysteresis effect whereby the overpressured zone could be in a stationary fractured or unfractured state.

2. Work in progress

In the time that remains we believe we shall find:

a. With periodic variations in input sediment rate or texture the fracture/healing oscillation can become entrained to a harmonic or subharmonic resonance or even respond chaotically.
b. In two and three dimensions, the oscillation will be very localized in space through one or a spatial array of local hydrofracture regions (rising fingers or "punctures"). The punctures will self-organize in a pattern in map view. A preliminary two-dimensional simulation is shown in Fig. 5 illustrating an overpressured compartment with fractured interior. A preliminary three-dimensional simulation has also been carried out.

C. Self-Arresting Flows

1. Work completed

A self-localizing feedback can occur when a fluid passes down a gradient of pressure due to the pressure dependence of reactions. An example is seen in Fig. 7 wherein we simulated (Chen et al., 1993) the precipitation of calcite. Due to the fluid pressure dependence of $CO_3^=$ protenation reactions and the calcite precipitation reaction, calcite tends to precipitate with a drop of pressure. If there is a small region of slightly lower permeability along the flow path, the pressure gradient will be greater there. This will cause greater precipitation there and hence lower permeability--further intensifying the local pressure gradient.

This is clearly a runaway effect. The localization of both pressure gradient and calcite precipitation gets increasingly more intense.

This phenomenon can lead to precipitation of bands of calcite in sandstones and may serve as a mechanism for developing efficient seals capable of sustaining large pressure gradients across them. It also serves as a mechanism for healing breached seals.

2. Work in progress

We are delineating conditions (imposed fluid composition, pH, salinity and temperature and rock mineralogy) favoring this phenomenon. We are investigating implications of this phenomenon in two and three dimensional systems and when organic solutes or fluids are present. The potential role of this phenomenon in sealing faults by uprising fluids to produce vertical, fault-associated seals is also being considered.

IV. RTM MODELS AND CONDITIONS FOR SELF-ORGANIZATION

Processes accounted for in our model are

* pressure solution via WFD, FFPD or hybrid models and associated compaction
* free face mineral reactions
* pore aqueous fluid reactions
* diffusion, dispersion and Darcy flow
* aqueous pore fluid compressibility and thermal expansion
* energy balance
* force balance and poroelastic or visco-plastic rock rheology
* pore fluid mass conservation
* hydrofracturing

The rates of these processes depend on a number of descriptive variables and therefore the dynamics of these systems is coupled. The rate laws are typically quadratic or otherwise nonlinear in the descriptive variables (concentrations, stress, temperature, etc.). Finally, the input of "reactant" sediment into the basin and the changes in stress, temperature and fluid pressure with burial, and thermal and tectonic history keep at least some of the processes far-from-equilibrium. The basin RTM system thereby satisfies all three necessary conditions for self-organization and nonlinear phenomena (Nicolis and Prigogine, 1977; Ortoleva et al., 1987a; Ortoleva, 1993a).

V. MATHEMATICAL AND NUMERICAL APPROACH

Technical challenges one encounters in such modeling studies are due to the enormity of the calculations. To meet them we are using homogenization theory, adaptive spatial gridding, specially designed linear solvers (preconditioned conjugate gradient-squared) and efficient procedures for handling systems of general chemistry. With this and parallel computation we are making the simulation of basin diagenesis in two and three spatial dimensions feasible.

A variety of mathematical techniques for the analysis of self-organization and nonlinear phenomena in RTM systems have been developed since the early 1970s by the principle investigator and others (see the monograph Ortoleva, 1992, for a review). In our studies of geochemical systems we have used a number of these techniques as outlined in the Table. These analytical approaches and experience strongly impact this project in providing analytical tests of the accuracy of our numerical simulations. They also ensure that numerical simulations are in keeping with results such as those obtained from bifurcation and matched asymptotic theories.

Because of the complexity of the problems of interest, our main emphasis has been on numerical solutions of the equations in favor of analytical results. Examples of results obtained are seen in Figs. 2-9.

Homogenization is a technique whereby one may rigorously calculate the average or large scale evolution of a system. In a basin we are often interested in the supra-kilometer scale variations in fluid pressure, stress or other state variable while it must be faced that sedimentary features, diagenetic bedding or other inhomogeneities are

present and can dramatically affect the large scale behavior. While simple averaging of variation of properties on the short scale can give completely incorrect results, homogenization theory yields rigorous long scale (averaged) equations. We are applying this technique to the analysis of basin-scale variations in pressure, diagenetic seals and fluid migration. Direct simulation on a grid capturing both the long and short scale variations would have been impossible.

The key to homogenization theory is the recognition that in many systems the short scale variations are roughly periodic or have a simple statistical character. This is often a reasonable assumption for many sedimentary or diagenetic layering features.

The homogenized basin RTM dynamics has been implemented. We have developed a parallel algorithm as the calculations are very parallelizable (Qin et al., 1993)--see Fig. 6.

Parallel algorithms are also being developed for our other RTM models used to generate Fig. 6. We believe that massively parallel architectures are ideally suited for basin RTM simulation. Massively parallel computation promises to foster in a new era in computational geochemistry.

The principal investigator's laboratory is equipped with an Intel iPSC/860 parallel supercomputer and a Sun multiprocessor system. These platforms and the lab's 5 Sparc (1, 2, 10) cluster are equipped with the PVM parallel software so that any or all of our computation power can be used on a single problem. Thus we have the computational facilities needed for this project.

VI. APPLICATIONS

In the course of our studies, we have developed practical RTM simulators. The simulators are very general and robust and therefore can be used to probe a range of system mineralogies, geometries, fluid chemistries, stress conditions, etc. They have front ends that allow the user to easily change among chemistries and the other variables. Through the use of specific RTM models and computational algorithms developed in this project these codes have been greatly advanced.

Our codes are presently used by four US major oil companies and companies in consortia in the US and Europe. They have built-in graphics, data banks and easy user modification of many of the specific phenomenological laws. Our codes are used in the analysis of problems for petroleum engineering (matrix acidizing (see Fig. 8) and steam flooding), exploration (defining conditions for preserving or creating reservoir rock, making diagenetic pressure seals and petroleum traps (see Fig. 9), predicting formation pressure and domains of tectonic fracturing in the basin (see Fig. 5)), and in the analysis of hazardous waste injection and storage in deep underground repositories and the fate of underground nuclear waste repositories.

The applications of our programs to industrial problems by our industrial supporters has actually introduced us to many of the self-organization and nonlinear phenomena that are the subject of this study.

All the efforts to make our codes practical research tools have paid for themselves through industrial funding. Having this extensive set of general modeling modules puts us in a very unique position to carry out our studies of self-organization and nonlinear phenomena in a wide range of realistic systems.

Mathematical Techniques Used and Developed by Ortoleva and Coworkers

for Geochemical Self-Organization and Nonlinear Problems

Technique ⇒ / Phenomena ⇓	Stability Analysis	Bifurcation Theory	Matched Asymptotics	Multiple Time Scales	Mode-Mode Coupling	Homogenization	Numerical Simulation
Reaction Front Fingering	2,6,8, 11,12, 16	6, 8, 10	12,55	13,59		74	12,13,14, 15,17,37, 41,64
Oscillatory Fluid Release via Fracture/ Healing							17,29,35, 68
Natural Convection in Basins					19		
Liesegang Banding	32,33, 38,43, 44,45, 46,69, 70			69			32,33,44, 46,62,69, 70
Stylolites and Diagenetic Bedding	40,45,4 7,48,58			20,58		4,65	18,20,21, 22,23,24 27,39,40 47,52,57, 58,65
Oscillatory Crystal Zoning		49		36			36
Crystal Shape Instability	3,4,7,9, 122						

Numbers refer to the bibliographic reference

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PROJECT OVERVIEW

PROJECT TITLE: Development of a Numerical Approach to the Study of Coupled Thermohydromechanical Processes in Geologic Media

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A. SPECIFIC PROJECT OBJECTIVES

Development and application of the numerical simulator ROCMAS for the analysis of thermal-hydraulic-mechanical processes in saturated fractured porous medium.

CURRENT WORK

The work involves development of the formulation equations and numerical algorithms that simulate the simultaneous occurrences of heat flow, fluid flow and deformation in the complex environment of geologic media. Coupled equations of conservation of mass, momentum and energy are used. The macroscopically formulated initial and boundary value problem is then developed into a finite element matrix algorithmic expression. The use of proper constitutive models that govern the macroscopic behavior of the media is a very critical aspect of this development. Realistic models of pre- and post-failure mechanical behavior of brittle and ductile continuum as well as fractured continuum, along with temperature-dependent fluid density and viscosity and stress-dependent fracture permeability are considered. Treatment of material nonlinearities, in the context of an incremental loading path, is another crucial part of the work. Alternative schemes of linearization, mainly based on the Newton-Raphson method, are employed.

PLANNED FUTURE WORK

Future work will be concentrated on the implementation of various material models to provide a more realistic and pragmatic representation of rocks. Equivalent anisotropic media and equivalent ubiquitously jointed media, with the related pre- and post-failure constitutive behavior, is of immediate interest. Implementation of proper macroscopic failure criteria, as opposed to the micro-fracture mechanics approaches, will prepare the ROCMAS code for a wide range of practical problems in the crust. New evidence of the role of fluids in faulting and earthquake mechanisms opens up new possibilities for ROCMAS applications.

B. HOW THIS PROJECT RELATES TO THE DOE MISSION

The mission of the Geosciences Research Program is to provide fundamental knowledge and understanding required to support the science and technology base needed

for improved current and future technologies aimed at better utilization and management of the Nation's energy resources and enhancing environmental quality. Many disciplines that are pursued to this end are interrelated. The intensity of this relationship depends (generally) to a great extent on the host environment. In may situations the host geologic materials are fractured to various degrees, mostly affecting the deformability of the media. In cases where discrete fractures or fracture zones are the major transport pathway, this issue of deformability may become critical to the degree that any analysis without due consideration for such phenomena may be invalid.

SCIENTIFIC AND TECHNICAL CONTENT

A. RELATION TO RESEARCH DONE BY OTHERS

This project is multidisciplinary research involving transport of mass, energy and momentum in geologic media. With the increasing desires for deep disposal of some industrial waste products, and concerns for proper use of resources and safe operations of geo-structures, a large number of organizations throughout the world are engaging in subsurface multidisciplinary research. An international forum for scientific exchange for such activities, called DECOVALEX, was initiated jointly by LBL and SKI of Sweden in 1990. This forum brings together participants abreast of the state-of-the-art in analysis capabilities of the coupled processes. Long term research in the areas of coupled processes has kept LBL efforts ahead of similar endeavors. The analysis approach chosen by most researchers is, so far, ad-hoc in that it involves linking of various, sometimes black box, tools designed for single phenomena analysis. Our work is based on direct solution of coupled phenomenological formulations.

B. MAJOR RESEARCH ACTIVITIES

As it is natural in works of this nature, a new development starts with theoretical development, algorithm formation, solution and verification. In the following we show the present status of our work in three phases of the ROCMAS simulator development.

1) Implementation of Material Models

We have successfully implemented calculation schemes to account for (a) elastoplastic, strain-softening, dilating discrete fractures, and (b) elastoplastic, strain softening, strain-hardening solid matrix. In addition temperature-dependent viscosity of the fluid is also accounted for in the new code.

2) The Implementation of Advanced Numerical Analysis Techniques

We have reorganized the code to replace the original solution scheme by an advanced method involving a mixed Newton-Raphson linearization scheme. Furthermore a newly developed sharp-front transport tracking method was also implemented. We expect the completely updated computer simulator will be among the most sophisticated and powerful codes for the study of coupled thermo-hydro-mechanical phenomena.

3) Verification and Application

The newly developed code has successfully undergone verification testing. We believe that the code is functioning as intended. The verified code has been applied to the design of a field experiment involving fluid injection into deformable fractures. The subsequent modeling study of field results indicates that the simulator has successfully modeled the hydromechanical phenomena involved in the experiment.

Our future plan will naturally involve similar phases. We need to develop the proper constitutive formulation for the new equivalent materials; we need to improve the linearization scheme in our solution; and finally, complete the effort with the verification and application phase.

C. ISSUES CURRENTLY BEING ADDRESSED

Having established the needed fundamentals in ROCMAS, we are concentrating on formulating various material models for randomly and homogeneously fractured rocks. Multiparameter inelastic equivalent solids and multilaminated continua are under consideration. Also, formulation of a proper approach for hydraulic constitutive behavior of such media is being investigated simultaneously. A search is also underway to optimize the existing linearization schemes to reducethe burden of CPU time in the analysis.

D. EXPERIMENTAL AND THEORETICAL APPROACH

Theoretical basis of our research involves formulation of proper momentum, mass and energy transport formulations expressing the thermohydromechanical phenomena in geologic media. Finite element formulation, linearization scheme, and material models implementations are the other main efforts.

Interest on the part of the Swedish Power Inspectorate (SKI) on other, but related, aspects of our development has led to a field experiment in Sweden. In this case fluid injection in deep fractures have provided opportunity for field verification of ROCMAS which has been reported. DECOVALEX international forum will provide other opportunities for experiments that will be used for field and laboratory verification of the ROCMAS code.

E. IMPORTANCE OF THE PROBLEM

In many applications such as nuclear waste disposal, geothermal reservoir development and hydrocarbon reservoir development (steam flooding) there is a strong coupling between mechanical, thermal and fluid flow behavior. ROCMAS computer code provides one of the very few predictive capabilities for a host of situations where the above conditions are encountered prevail.

PROJECT OUTPUT

A. MAJOR ACCOMPLISHMENTS

1. An algorithm for handling fast moving sharp-front transport problems in finite element numerical solutions has been developed. By employing this new and easily implemented procedures, the performance of the simple Galerkin finite element transport solutions improve dramatically. This development puts finite element, in one of the very few areas where it suffered major weakness, ahead of the widely used upstream finite differences.

2. A experimental field verification of the code performance has been achieved. We have successfully modeled a series of fluid injections into deep fractures in an experimental well in a rock mechanic laboratory at the University of Luleä, Sweden.

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STABLE ISOTOPE SYSTEMATICS OF FLUID/ROCK INTERACTION

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INTRODUCTION

Determination of the distribution of the stable isotopes of O-H-C-S in fluids and minerals has become a standard and extremely powerful approach in elucidating the temperatures, material fluxes, rock and fluid origins, and time scales associated with ancient and active fluid-rock interaction in the Earth's crust. A great deal of progress has been made in determining the equilibrium fractionations of $^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, and $^{34}S/^{32}S$ among fluid and mineral components at high temperatures (>400°C), from both experimental exchange studies and theoretical calculations. However, it is well known that theoretical calculations do not extrapolate well to low temperature conditions, and sluggish reaction kinetics have severely limited the data base of isotope exchange experiments for many mineral and fluid species in the 20-400°C range. This is particularly problematic in addressing geoscience issues relevant to the Department of Energy, because geothermal and hydrocarbon energy resources are a direct result of fluid-rock interactions and fluid migration processes at temperatures in the 50-400°C range. Similarly, shallow to deep toxic and radioactive waste disposal strategies will invariably involve the monitoring and/or prediction of groundwater fluxes through the waste form at ambient conditions.

Compounding this problem of a lack of adequate low-temperature isotope fractionation factors, is the recognition, from studies of natural systems, that mineral assemblages clearly out of isotopic equilibrium or yielding isotopic temperatures inconsistent with those estimated from phase equilibria or fluid inclusion evidence are more widespread than previously realized. Collectively, these studies indicate that (1) isotopic disequilibrium can occur at high as well as low temperatures, (2) different minerals exhibit varying susceptibilities to retrograde exchange (e.g., feldspars versus quartz), and (3) the mechanisms of isotope exchange are varied and depend on the geochemical conditions (e.g., fluid chemistry, temperature). Therefore, critical to the interpretation of the extent of isotope equilibrium in natural systems is the knowledge of the rates and mechanisms of isotope exchange between rock (minerals) and fluids.

OBJECTIVE

It is clear that the available experimental equilibrium and kinetic isotope exchange data are insufficient to permit accurate quantitative modeling of many mineral-fluid systems in the temperature and pressure ranges relevant for geothermal and hydrocarbon resources. To address this problem, project personnel are actively engaged in experimentation that is designed to elucidate the mechanisms and rates of isotope exchange of select mineral-fluid reactions. Additionally, natural hydrothermal systems are being examined in order to test whether isotope equilibrium has been attained. As an outgrowth of these studies, we have initiated research on the behavior of stable isotopes at low temperatures in environments where interactions involve soil-atmosphere-groundwater. Studies on experimental equilibrium isotope fractionation are cur-

rently being conducted in another DOE/OBES Geosciences' funded program. The research "tasks" pertinent to this project are summarized in the paragraphs below.

TASK I. Experimental Studies of Isotope Exchange Rates In Mineral-Fluid Systems

Granite-Fluid Isotope Exchange - Variations with time in the alteration mineralogy and oxygen isotopic composition of solutions, minerals, and rocks have been experimentally investigated in the systems: granite-H_2O±NaCL±KCl at temperatures of 170 to 300°C, pressures from L/V saturation to 0.3 kbars, water/rock mass ratios of 0.2 to 6, and grain sizes of ~0.1 to 2.5 mm for periods up to 1006 hours. Alteration assemblages formed in the experiments are dominated by chlorite (after biotite), sericite-zeolite-albite (after K-feldspar and plagioclase), and hematite (after magnetite and pyrite). The abundance of these minerals continued to increase with increasing reaction time, temperature, NaCl (or KCl) concentration, and surface area of solids. Major element concentrations, however, attained steady state in less than 330 hours. Reaction of rock ($\delta^{18}O_i$ ~ +8‰) and aqueous solutions ($\delta^{18}O_i$ ~ -10‰) resulted in depletion of ^{18}O in the solid and enrichment of ^{18}O in the fluid. The magnetudes of change increase as temperature, time, salt concentration, and surface area increase. The trends in isotopic shifts are directly related to changes in the style and intensity of mineralogic alterations in the granite. The degree of isotope exchange in the experimental systems between granite (minerals) and solutions was computed from the comparison with calculated equilibrium fractionation factors and ranges from less than 5 to 50‰. The oxygen isotopic changes were observed to follow closely with those expected from a first-order rate law. At temperatures between 170 and 300°C, rate constants for oxygen isotope exchange between granite and pure water range from 10^{-9} to $10^{-8.1}$ (moles O m^{-2} s^{-1}) whereas rates in the granite-0.1 m NaCl system range from $10^{-8.5}$ to $10^{-7.6}$. Rate constants were also retrieved for biotite, K-feldspar and plagioclase interacted with either pure water or 0.1 - 1 m NaCl.

Calcite-H_2O-NaCl Isotope Exchange - Variations in the extent of oxygen isotope exchange (F, where F = 0 at t = 0; and F=1 at t = ∞) have been measured in the system calcite-H_2O-NaCl as a function of temperature, pressure and concentration of NaCl. The conditions of these hydrothermal experiments are: T=300-600°C, P=1 kbar (0.25 kbar at 300°C; and 0.55,1 and 2 kbars at 500°C only), m NaCl=0, 0.1, 0.3, 1,and 4, solution/calcite mass ratios ~4, and run durations=211-1956 hours. There is a pronounced increase in the F-values with increasing temperature, salinity, pressure (500°C only), and degree of grain rounding and regrowth. The rate of change in F is initially steep but tends to flatten out with increasing NaCl at ≥ 1m **(Fig 1).** This greater degree of recrystallization is probably related to the enhanced solubility of calcite in the presence of NaCl. Data at 500°C exhibit a trend of increasing F with increasing pressure.

Rate constants (log r in moles O m^{-2} s^{-1}) calculated from these data range from a maximum value of -6.75 at 600°C, 1 kbar, 4 m NaCl to a minimum rate of -9.46 at 300°C, 0.25 kbar, 0 m NaCl. Activation energies were calculated for each NaCl concentration at 1 kbar and vary as 15, 16, 19, 20 and 19 kcal $mol^{-1}$for 0, 0.1, 0.3, 1 and 4 m NaCl, respectively. Volumes of activation ($\Delta V^{\neq}$) estimated from the 500°C pressure data range from -40 to -9 cm^3 mol^{-1} for 0 and 4 m NaCl, respectively. These data suggest that solvation of ions in solution during the activation step is the dominant process influenced by pressure. Model calculations indicate that isotopic equilibration times are very rapid, on the order of 10's to 100's of years at high temperature (>500°C), high salinity (>1m) and high pressure (>1 kbar), depending on the solution to solid ratio and initial grain size.

Calcite-H_2O-CO_2 Isotope Exchange - In order to examine the effect of mixed-fluid composition on the rates and mechanisms of carbon and oxygen isotope exchange, we have conducted experiments from 300°C, 0.25 kbar to 700°C, 1 kbar at % XCO_2 = 0, 2, 4, 5, 11, 18 and 100. A minimum of four runs lasting 72-1200 hours were used at each P, T, X condition to constrain the time dependence of isotopic exchange. The experimental conditions cover a wide range in calcite solubility and CO_2-H_2O miscibility, and re-examine the $CaCO_3$-CO_2 and $CaCO_3$-H_2O subsystems. SEM observations demonstrate that essentially no grain growth occurs when CO_2 is present in any amount, even at 700°C, whereas recrystallization and

growth in pure H_2O is extensive, in support of previous pseudo-first order models for calcite-water. Based on SEM observations, we have modeled carbon and oxygen isotope exchange using a combination of diffusion and surface reaction rate models. Preliminary analysis of the data indicate the following: (1) carbon isotope exchange occurs primarily by diffusion, even at 700°C, 1 kbar and $\%XCO_2$=2, (2) the effective ^{13}C diffusion coefficient decreases with increasing XCO_2 - e.g., D~$1X10^{-15}$ at % XCO_2=2 to ~$1X10^{-16}$ $cm^2\ s^{-1}$ at % XCO_2 =100, (3) oxygen isotope exchange is faster than carbon for all XCO_2, by more than one order of magnetude in some cases, (4) oxygen exchange rates in pure H_2O are much faster than in H_2O + CO_2, except at 300°C, and (5) annealing of grains at long durations leads to lower fractions of ex-change (F) than predicted from initial rates due to a reduction of specific surface area and elimination of defects.

The Relationship Between Mineral Chemistry and Isotope Exchange Rates - Oxygen isotope exchange between minerals and fluids in systems far from chemical equilibrium are controlled largely by surface reactions such as dissolution-redeposition or transformation of one phase to another. This behavior can be adequately modeled by a simple pseudo-first order rate model that assumes the rate limiting step involves the addition and removal of oxygen atoms from the surface. Oxygen isotope rate constants calculated from a variety of partial exchange experiments can be ranked in the following approximate order: carbonates ≥ sulfates > tekto > phyllo > ino > sorosilicates. Interestingly, this order for silicates follows an increase in the ratio of non-bridging oxygens to tetrahedral cations. Calculated activation parameters (E_a vs A_O) for these reactions can be partitioned into distinct linear trends dependent on the mineral type - i.e., separate trajectories for sulfates, carbonates and silicates in E_a vs A_O space (**Fig 2**). Data distributed along any given mineral trend are controlled by the cation type. There is an excellent linear correlation between increasing oxygen isotope rate constants and cation radii for a given mineral system at T's>300°C. For example, in the carbonate system, the rates can be ranked in order: Ba (1.43Å) >Sr (1.13Å) >Ca (0.99Å). Silicates also exhibit a similar linear behavior at high T's, where the ranking of rates is: Ksp(K:1.33Å) > Ab(Na:0.98 Å) ≥ Woll (Ca:0.99Å) > Diop (Ca/[Mg:0.65Å]) >Zoisite (Ca/[Al:0.5 Å]). This progression correlates well with the decrease in the radii of the cation or cation "pair". These observations are analogous to those of Casey and Westrich (1992) who showed linear correlations among increasing divalent cation radii (Ca>Mg>Be), increasing dissolution rate of nesosilicates, and increasing rate of water exchange from the solvent into hydration spheres of corresponding dissolved cations. Consideration of the isotope rate data in this context suggests the possibility of a link between oxygen isotope exchange accompanying surface reaction and mechanisms by which dissolved cations exchange ligands in solution, and become solvated. Currently, we are examining other correlation schemes that could lead to a greater predictive capability in estimating rates in the absence of hydrothermal experiments.

TASK II. Stable Isotope Studies of Natural Hydrothermal Systems

Degree of Oxygen Isotope Exchange in Hydrothermal Systems - The close agreement between oxygen isotope temperatures and measured bore-hole temperatures for a majority of geothermal systems (e.g., Iceland: Roosevelt Hot Sps, UT; Wairakei; Broadlands; Waiotapu; Valles, N. Mex.; Cerro Prieto; Salton Sea) examined indicates that the fluids and alteration mineralogy are temporally related. The fact most secondary phases in these hydrothermal systems are isotopically equilibrated with the aquifer fluids is consistent with species distribution and mass transfer calculations that indicate that chemical equilibrium has also been attained. However, it is clear from a comparison of measured bulk rock-fluid oxygen isotope fractionation factors with calculated "altered" rock-fluid equilibrium fractionation factors, that many systems - geothermal and vein-epithermal alike - exhibit varying degrees of fluid-rock oxygen isotope equilibration. This result is in accord with observations made by Helgeson (1971), who proposed the idea of local equilibrium for small, mineral-fluid domains.

For any given hydrothermal system, the typical deviations in minimum and maximum rock-fluid isotope fractionation, referenced against estimated equilibrium fractionation factors, range

from a few per mil to over 10 per mil, respectively. By quantifying the initial, final and equilibrium rock-fluid fractionation factors, estimates are made of the fraction of exchange(F) using the Northrop-Clayton (1966) expression. Values for F fall between 0.25 and 1.0 (i.e., equilibrated) for the hydrothermal systems considered, with each system exhibiting its own distinct range. Even with a consideration of errors on the order of either ±25 to 40°C in measured (or inferred temperature), or 1 to 2 per mil in α values, significant deviations from isotopic equilibrium are still preserved. From this analysis, a systematic trend was observed for most of the geothermal and vein-epithermal systems, wherein the degree of exchange increased with increasing salinity and temperature(**Fig 3**). This behavior is consistent with results obtained from rock(mineral)-fluid isotope exchange experiments (e.g., Cole et al., 1987; 1992). Using published oxygen isotope exchange rate data, calculations indicate that the F-temperature-salinity trends observed in these natural systems are compatible with a simple, closed-system model that evaluates F as a function of temperature, rock type, grain size, W/R ratio, salinity, and duration of interaction.

The results of this study suggest that small-scale isotope disequilibrium in many hydrothermal systems may have resulted from local, self-sealing of the fracture (or pore) network prior to attainment of final isotope (or chemical) equilibrium. Final isotopic (and chemical) equilibration is probably only achieved under conditions where fractures (or pores) remain open or continue to propogate during fluid-rock interaction at elevated temperatures. For systems exhibiting disequilibrium, the flow porosity was likely sealed off, and/or the thermal regime had declined in magnitude to a level where alteration reactions were too slow to produce significant secondary mineral formation and associated isotope exchange.

Isotopic Evolution of the Organ Mountain Caldera and Batholith, N. Mex. - The early Oligocene Organ caldera consists of large silicic ash-flow tuffs and trachytic lavas, and overlies an exposed comagmatic batholith. Recent field, petrographic, and geochemical studies suggest that the intracaldera volcanics were derived largely from the upper-most portions of the zoned magma body. The largest volume phase of the batholith is the compositionally zoned (55 to 75% SiO_2) Organ Needle pluton. The most mafic part of the pluton is a monzodiorite with $\varepsilon_{Nd,t}$ = -2.8 and $^{87}Sr/^{86}Sr_t$ = 0.7047. These values are consistent with a primitive, isotopically depleted or young mafic (<55% SiO_2) parental magma source. ε_{Nd} (-4 to -14) and ε_{Sr} (+30 to +120) variations exhibited by the Organ volcanics are similar to those of continental margin volcanic rocks, and suggest that mixing (modified by fractional crystallization) occurred between primitive arc-type material and the crustal rocks through which these primitive magmas had to pass. $\delta^{18}O$ - $^{87}Sr/^{86}Sr$ relationships support this view, but also reveal that fractional crystallization has played a role in modifying the isotopic and elemental signatures of these rocks. In addition to delineating complex mixing-crystallization behavior, the O and H isotope data indicate that portions of the pluton have interacted hydrothermally with isotopically-light meteoric water. The average δD of the granitic rocks is -105‰, which is approximately 10 ‰ lighter than the lightest values assumed for average, unaltered igneous rocks (~ -95‰). Depletion of D/H (to a low of -114‰) is more pervasive than depletion of ^{18}O, which is only observed in alkali granites, the latest phase of the Organ Needle pluton. These relatively fresh looking rocks have $\delta^{18}O$ values as low as 3‰. The volcanic equivalents to the pluton phases exhibit a pronounced depletion in δD (-95 to -130‰) with decreasing water content (0.47 to 0.1 wt. %), indicative of open-system degassing typically observed in many felsic magma systems (e.g., Long Valley, CA.).

Isotopic Studies of Fluid-Rock Interaction in the Appalachians - Carbon and oxygen isotopes have been used in conjunction with petrologic and trace element geochemical studies to provide insight into the nature of fluid-rock interaction in several central and southern Appalachian hydrothermal systems as part of CSDP activities - i.e., ADCOH and potential drilling for unconventional sources of methane. In the Carolina volcanic slate belt (CVSB), volcanogenic mineral deposits include polymetallic massive sulfide (in volcanic host) and disseminated gold-pyrite deposits (in sediment host) in proximal and vent facies, metavolcaniclastic and meta-epiclastic rocks of a magmatic arc succession. The $\delta^{18}O$ variation of CVSB rocks with SiO_2 resembles that from modern, continental-margin magmatic arcs. Significantly, there is a profound separation in $\delta^{18}O$ values between the lower volcanic -dominated and the upper,

sediment-rich successions. The volcano-sedimentary transition is marked by a profound shift of 3-5‰ in $\delta^{18}O$. Alteration assemblages have similar oxygen isotope signatures to the host rocks, although they are clearly effected by alteration processes. Pyrophyllite-rich rocks from the lower section exhibit $\delta^{18}O$ values from -0.1 to 7.2‰, whereas pyrophyllite-bearing sediments in the upper section have $\delta^{18}O$ values ranging from 7.3 to 10‰. These data demonstrate that the transition from subaerial, meteoric- to submarine, seawater-dominated hydrothermal systems marks a change in metallogenesis and is preserved through lower greenschist metamorphism.

Isotope techniques have also been used to investigate the mobility of methane-bearing fluids during amphibolite-grade meatmorphism in the northern Alabama Piedmont. Carbon and oxygen isotopes in the synmetamorphic Rockford granite and its graphitic metasedimentary host rocks clearly indicate large scale mobility of methane-bearing (10-15 mole %) fluids and high fluid/rock ratios at conditiions of 500-600°C and 4-5 kbars. These results demonstrate that both the generation and migration of methane by reaction of reduced carbon in sediments with metamorphic fluids can occur at any T and P up to the onset of partial melting of the rock.

TASK III. Paleoclimate Controls on Carbon and Oxygen Isotopes in Low Temperature Systems

Paleoclimate Controls on $\delta^{18}O$ and $\delta^{13}C$ in Caliche of early Permian Age - The oxygen and carbon isotopic compositions of caliche in fluvial and supratidal rocks of the Abo formation (early Permain), south-central N. Mex., are controlled by paleoclimate and depositional environment. Oxygen isotopes are similar in the fluvial and supratidal caliches and range from 21.6 to 30.5‰ (SMOW). The data exhibit a crude bimodality and $\delta^{18}O$ enrichment with a decrease in age (higher in the section). Consideration of these data in the context of δ-temperature relations suggests that (1) surface waters responsible for caliche formation increased in $\delta^{18}O$ (from roughly -8 to +1‰) over the 18 m.y. time interval that separated the lowest stratigraphic nodule horizon from the highest, (2) the increasing $\delta^{18}O$ values also reflect a warming trend (approximately 15 to 30°C) in the mean monthly temperature over this same time period, with perhaps an associated increase in Permian ocean temperatures, and (3) the significant variation in $\delta^{18}O$ from oldest to youngest caliche was probably enhanced by the "amount" effect, such that as the temperature increased, the amount of precipitation decreased resulting in high $\delta^{18}O$ values.

Caliches in the Abo are enriched in heavy carbon (-7.2 to -1.5‰ PDB) compared to that of soil carbonate derived exclusively from C_3 plants (-12‰ PDB), and the supratidal caliches contain somewhat heavier carbon compared to the fluvial caliches. The $\delta^{13}C$ values for both environments increase with a decrease in caliche age. These results indicate that as the temperature increased and rainfall decreased with time, the level of C_3 plant productivity declined, allowing a greater influx of atmospheric CO_2 into the soil (**Fig. 4**). This can only occur when soil respiration rates are quite low or at very shallow depths (less than 10 cm), or both.

Plio-Pleistocene Paleoclimate in the Southern Rio Grande Rift, N. Mex. - Oxygen and carbon isotopes of pedogenic carbonate provide a detailed record of paleoclimate changes from late Pliocene through early Pleistocene in the Rio Grande rift of south-central N. Mex. A total of 30 calcic paleosols were sampled at three stratigraphic sections of the fluvial facies of the Camp Rice Formation and one calcic paleosol was sampled from fluvial sediment inset against the Camp Rice Formation. Reversal magnetostratigraphy at all four sample sites bracket the age of the paleosol-bearing strata between 3.4 and 0.7 Ma and allow estimates of the absolute age of individual paleosols.

Three paleoclimatic stages are indicated by the carbon and oxygen isotopic data from south-central N. Mex. The initial stage, from 3.1 to 2.5 Ma, was characterized by the overall lowest values of $\delta^{18}O$ and $\delta^{13}C$ and by an increase in isotope values with decreasing age, suggesting high effective moisture and abundant winter precipitation, which decreased through time, and/or relatively low temperature, which increased through time. The second stage (2.5 to 1.4 Ma) displays an increase in $\delta^{18}O$ with decreasing age, but no significant change in $\delta^{13}C$ with time, suggesting that the effective moisture was nearly constant, but that temperature and/or summer precipitation may have increased through time. The final stage (1.4 to 0.8 Ma) shows an overall

increase in both $\delta^{18}O$ and $\delta^{13}C$ with decreasing age, corresponding to less effective moisture, higher temperature, and/or greater summer precipitation through time. Plio-Pleostocene paleoclimate changes in south-central N. Mex. correlate with paleoclimatic data elsewhere in the southwestern U.S. and adjacent Great Plains, and may have been influenced by the onset of Northern Hemisphere continental glaciation, rise of the Sierra Nevada and Transverse Ranges, and/or broad regional uplift of the western U.S.

Late Quaternary Paleosols and Climate Change in Southern New Mexico - Multiple generations of alluvial fans surround arid mountains in southern New Mexico. Radiocarbon dates of charcoal indicate that the youngest generation of fans were deposited after 7 ka. These Holocene deposits bury fans of Late Pleistocene age. Well-preserved paleosols associated with the alluvial fans contain an isotopic and palynologic record that indicates the Holocene fans were produced by erosion-sedimentation events caused by climate change. Carbon isotopes in pedogenic carbonates are isotopically heavier in the late Pleistocene paleosols, ranging from -3.3 to -0.6‰ (PDB). In contrast, Holocene paleosols contain lower $\delta^{13}C$ values, ranging from -10.1 to -5.8‰ (PDB). The change from heavy to lighter carbon isotope values occurs rather abruptly at about 9000 ka. The higher $\delta^{13}C$ values in the late Pleistocene may reflect abundant C_4 grasses, which would have curtailed erosion. The lower $\delta^{13}C$ values in Holocene soils may indicate the decline of grasslands, and a shift toward desertscrub and greater erosion. Pollen analyses of paleosols supports this interpretation. Late Pleistocene paleosols contain abundant Gramineae pollen, and lack mesquite or creosote pollen. Holocene soils, on the other hand, contain significantly less Gramineae pollen and an increase in saltbrush, mesquite and creosote pollen. The $\delta^{18}O$ values are similar for Holocene (-6.1 to -4.0 vs SMOW) and late Pleistocene (-5.6 to -4.8 vs SMOW) paleosols, with an overall average of about -5.0‰ (±1.0‰). Using currently accepted paleotemperature models, this average value reflects a mean annual temperature of roughly 13.8°C, or approximately 57°F, which apparently did not change significantly over the last 40 ka. The question remains, however, as to what kind of paleoclimatic conditions caused the vegetation changes around 9 ka? One obvious possiblility is a decrease in rainfall that imposed a stressed environment on this area, within which only the hardiest of plants could survive, such as the desertscrub. With a loss of the grasses, weathering could become more accelerated. Another intriguing idea involves the nature of atmospheric CO_2 during this time frame. From polar ice core data, we know that the gobal CO_2 content increased dramatically from about 180 ppmv to roughly 280 ppmv from about 14 ka to 10 ka. By itself, this may be only coincidental. However, it is known that many C_4 species can not tolerate high CO_2 contents, and still efficiently process CO_2 photosynthetically. It is possible that a combination of less rainfall and high CO_2 led to the decline of C_4 vegetation in the southwest. Futher work is being conducted to test these ideas.

PROJECT OUTPUT

A. Major Accomplishments

(1) Rates of oxygen isotope exchange have been measured in the following systems - granite-H_2O-NaCl-KCl and calcite-H_2O-NaCl. Carbon and oxygen isotope exchange rates have been measured in the system calcite-H_2O-CO_2. These rate data, coupled with detailed physical characterization of the run products (e.g., SEM) provide valuable insight into the mechanisms of isotope exchange, and form the basis for quantifying the duration of fluid-rock interaction for systems whose lithologies are analogous to those studied experimentally. Additionally, important correlations have been observed between the rate data (and activation parameters) and various mineral chemistry parameters, such as cation radius and the ratio of non-bridging oxygens to tetrahedrally coordination cations.

(2) In addition to demonstrating the valuable role stable isotopes play in quantifying paleo-

temperatures and sources of fluids in a number hydrothermal , metamorphic and igneous systems, we have documented evidence of widespread oxygen isotope disequilbrium between rocks and fluids, particularly in geothermal systems and their fossil analogs. Data from these systems indicate that the degree of isotopic equilibration increases with increasing temperature, salinity, and fracture intensity. The rate data obtained in this project (item 1) can be used to put constraints on the duration of fluid-rock interaction.

(3) Carbon and oxygen isotope compositions of pedogenic carbonates in paleoosols or caliche have provided the basis for paleoclimate reconstructions of a number of different geologic time intervals - i.e., early Permian, middle Pliocene - early Pleistocene, and late Pleistocene - Holocene. Some of the more significant results include (a) the demonstartion of a warming trend in the early Permain (at least in the SW U.S.), signaling the onset of what would become a time of evaporation and formation of restricted marine basins (e.g., Delaware Basin), and (b) the docmentation of a dramatic shift in carbon isotope values (from heavy to light by ~6 to 8‰) in pedogenic carbonates at about 9,000 ka signaling the decline of C_4 grasslands and the spread of C_3 desertscrub species in south-central N. Mex., due to a decrease in moisture and/or increase in global CO_2.

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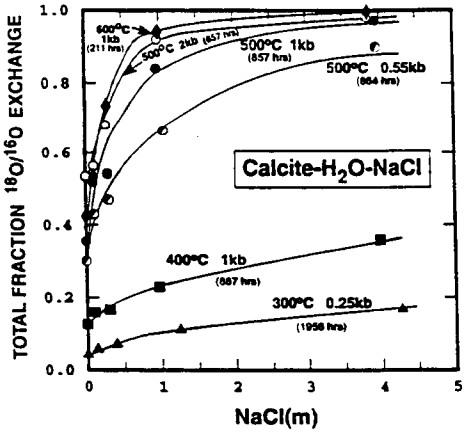

Fig. 1 Fraction of $^{18}O/^{16}O$ exchange vs. NaCl molality.

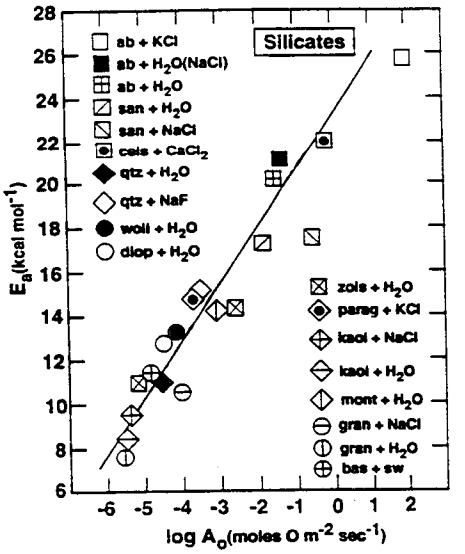

Fig. 2 Activation parameters for oxygen isotope exchange controlled by surface reactions.

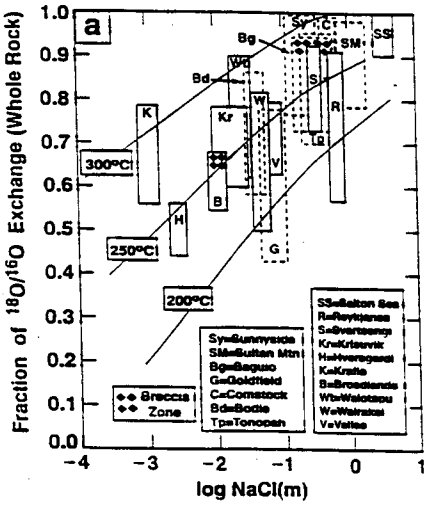

Fig. 3 Fraction of $^{18}O/^{16}O$ exchange between whole rocks and fluids of varying salinity from natural hydrothermal systems.

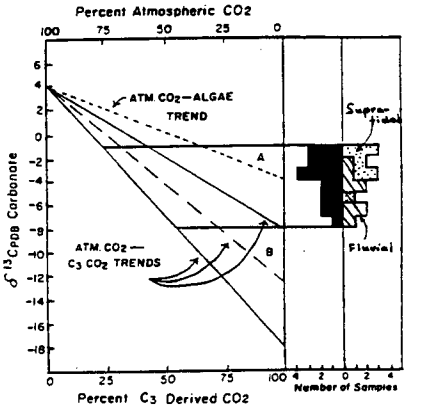

Fig. 4 Two-component mixing diagram of soil carbonate formed in isotopic equilibrium with soil CO_2 for Permian-age soil nodules.

DOE GEOSCIENCE WORKSHOP
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1. PROJECT TITLE DOE FG03-90ER14154
Fluid flow, element migration, and petrotectonic evolution of the early Mesozoic central Klamath island arc, northwesternmost California

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5. SCIENTIFIC AND TECHNICAL CONTENT

A. Research in various portions of the central Klamaths is being undertaken by others, including Allan Kays at the University of Oregon, Mary Donato of the USGS, Mark Helper at the University of Texas, Greg Harper at SUNY/Albany, Jason Saleeby at Caltech, and Cal Barnes at Texas Tech. To lesser or greater degrees, all researchers are studying the geology, petrotectonics, and geochronology of various portions of this mountain belt in an attempt to unravel its accretionary origin. The work supported by the DOE and conducted by the P.I. and his associates interfaces with, and builds on these studies of laterally contiguous areas. The attempt involves integration of these advances in our knowledge of a well-exposed immature island arc in order to determine its detailed thermal structure and evolution with time. Results should be applicable to other Circum-Pacific island arcs and convergent continental margins.

B. The research schedule requires the nearly simultaneous mapping and continuation of petrologic, structural, and geochemical investigations in order to enhance scientific feedback, and thereby to understand better the origin and evolution of the lithotectonic belts. Future efforts will focus on regional-scale geologic relationships, and on detailed fluid-rock exchanges (both in terms of element chemistry and stable isotopes) at shallow and intermediate levels in the arc edifice.

C. Critical, interrelated scientific questions being addressed for the Klamath oceanic arc include the following: How did pressure, temperature, and the activities of volatile components vary as a function of time? Where did the fluids originate? What are the genetic and deformational relationships among the arc and its neighboring lithotectonic units? What is the detailed structure of the uppermost portions of the Klamath terrane assembly? How did these structures control fluid flow and associated advective heat transfer? What was the geochemical nature of fluid-rock interaction within the zone of fracture? And finally, what

was the quantitative timing of the major plate tectonic events, including deformation, volcanism, igneous intrusion, metamorphism, fluid expulsion, and exhumation?

D. An integrated study is underway, employing all of the following techniques: detailed local field geologic mapping at a scale of 1:24,000 and larger; regional lithotectonic reconnaissance and compilation at 1:200,000; bulk-rock XRF analysis; electron microprobe analysis of coexisting phases; mass spectrometric analysis of minerals ($^{40}Ar/^{39}Ar$; $^{18}O/^{16}O$) and of bulk rocks ($^{18}O/^{16}O$). It has been our experience that each technique allows the formalization of specific constraints on the origin and evolution of this arc system; in aggregate, the integrated attack provides a fuller appreciation of the development of the entire Klamath province.

E. Few composite but intact island arcs are as well-exposed at intermediate and upper crustal levels as is the study area. Accordingly, knowledge obtained in the Klamaths should be readily applicable to older and more dismembered oceanic arcs, and to as yet unexposed modern arcs. Because of their high heat flow, such geologic regimes are appropriate targets for geothermal power generation. Shallow levels of such arcs represent suitable case histories for studying rock fracture, fluid migration, and hydrothermal metasomatism.

6. PROJECT OUTPUT

A. Investigations in the central Klamath Mountains supported by DOE FG03-90ER14154 have documented the presence of a polymetamorphosed suite of highly magnesian basaltic rocks in the Sawyers Bar terrane of the western Triassic and Paleozoic belt. These metavolcanics display apparent komatiitic chemical affinities. The metabasalts were initially thought to reflect the Permo-Triassic to Middle Jurassic overriding of an oceanic hot spot by the stable, non-subducted arc-capped North American lithospheric plate, but are now regarded as variably-cumulate, hornblende-phyric porphyries. The mafic flows represent metasomatized and metamorphosed, immature Salmon River arc basalts (IATs), and interlayered, mildly alkaline North Fork oceanic island lavas (OIBs), possibly erupted following subduction of a spreading center. These igneous rocks are intercalated with and are interpreted to predominantly overlie distal turbidites. The superjacent assemblage was laid down, altered and recrystallized in an immature island arc setting during the hypothesized collapse of a Philippine Sea-type back-arc basin which brought the westerly Sawyers Bar oceanic arc terrane into juxtaposition with an inboard, pre-existing Stuart Fork subduction complex and yet more easterly Klamath terranes. At about the same time, an outboard, active calc-alkaline arc, the Western Hayfork terrane, was encroaching eastward due to contraction and suturing against the intervening and collapsing Eastern Hayfork unit (Hacker and Ernst, 1993).

In-progress research has concentrated on elucidating the areal extent and structural/stratigraphic relations of these mafic metavolcanic units, and has documented the insignificant degree of crustal contamination of the melts by associated terrigenous metasediments. The physical conditions of metamorphism and of aqueous fluid-rock interaction accompanying island-arc accretion have been determined as follows: Middle Jurassic regional metamorphism of the Sawyers Bar/Stuart Fork amalgamated terrane took place at 350-500°C and 2.5-4.0 kbar; contact aureoles peripheral to the mid-Jurassic calc-alkaline plutons reached maximum physical conditions of 500-600°C at 2.0-3.0 kbar; somewhat earlier sea-floor exchange, followed by greenschist facies regional recrystallization, and later contact metamorphism in aggregate have resulted in an increase of $\delta^{18}O/^{16}O$ from igneous values presumably near +6 to present bulk-rock values ranging from +10 to +15. Intrusion of the post-collisional granitoids mobilized alkalies, silica, and especially oxygen isotopes in the sedimentary strata intimately interlayered with the IAT (Salmon River) and OIB (North Fork) greenstones, overprinting the effects of an inferred earlier submarine alteration in the mafic volcanics. Several sets of temporally overlapping mafic dike/sill series have been intruded into the amalgamated complex (Ernst, 1993), reflecting longterm orogenic magmatism.

The thermal structure and its evolution in the central Klamath Mountains evidently reflect surfaceward advective transport of magmatic energy derived from the partly fused downgoing oceanic slab + overlying mantle, as well as hydrothermal fluid circulation. Limited Nd-Sm isotopic data for the mafic metavolcanics suggest the lack of remobilization of, or contamination by, old sialic crust. Clarification of the thermal evolution of this crust-constructional event in the immature, basaltic island arc is the goal of the research now underway, employing both field and geochemical methods. What has recently been documented by new radiometric data is that two volcanic/plutonic arcs were active contemporaneously at about 170 Ma in the central Klamaths — the outboard Western Hayfork, and the inboard (continentalward) Sawyers Bar (Hacker et al., 1993). Furthermore, within the eastern terrane, eruption of the North Fork and Salmon River volcanics overlapped each other and the initiation of calc-alkaline plutonism as well (Ernst, 1993).

Continuing work by Hacker and Ernst is documenting the flow and P-T history of aqueous fluids through the evolving Klamath arc, utilizing electron microprobe and oxygen isotopic data. We have nearly finished a regional reconnaissance map showing the distribtion of the OIB and the IAT lavas throughout the California part of the Klamath Mountains (Hacker, et al., in review). Applications of the terrane concept to the central Klamath Mountains and northern Sierra Nevada have also been re-evaluated in the light of regional petrotectonic and metamorphic relationships (Hacker, et al., 1993; Hacker and

Ernst, 1993; Hacker, 1993). Investigations of the regional and contact metamorphism/ metasomatism of the Sawyers Bar metasedimentary pile are in progress. Another work, a new geologic map of the Sawyers Bar area at a scale of 1:48,000, is approaching completion (Ernst, in preparation). A regional compilation at 1:200,000 of the terrane amalgamation and metamorphic facies distribution in the entire Klamath Mountain province is also underway (Hacker and Ernst, 1992, and in preparation).

Additional central Klamath samples have been collected from the southern Marble Mountain amphibolitic assembly, the greenschistic Sawyers Bar terrane, and the feebly-recrystallized Pony Camp mafic volcanoplutonic complex for intermediate- and shallow-level water-rock interaction studies, utilizing stable isotope fractionation. This project is being pursued in cooperation with Yehoshua Kolodny (The Hebrew University) and Mark Barton (The University of Arizona); its goal is to shed light on contrasting water-rock interations at high and middle levels of this oceanic island arc.

In an experimental study of metamorphic transformation rates, Hacker, et al. (1992) have investigated the calcite-aragonite reaction in polycrystalline marbles. Hacker and Peacock (in review) have also discussed the generation, preservation, and exhumation of deeply subducted crustal rocks in another work. These principle-oriented studies, while less central to the major thrust of the Klamath project, also deal with the P-T evolution of subducted rocks.

Many of our Klamath projects are still underway, but it should be clear that the attempt here is to broadly relate the thermal evolution of the upper portion of a well-exposed oceanic arc through local and regional mapping, petrologic and geochemical studies of rocks and constituent minerals, documentation of fluid-rock interactions, and elucidation of the tectonic history of this belt.

B. DOE-Supported Productivity

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(2) Hacker, B.R., and Ernst, W.G., 1992, Preliminary metamorphic map of the Klamath Mountains, NW California and SW Oregon: Geol. Soc. Amer. Abstracts with Programs **24**, no. 7, 292.

(3) Ernst, W.G., 1993, Chemically distinct diabasic dike/sill sequences of contrasting ages, Sawyers Bar area, central Klamath Mountains, northern California: Jour. Petrology **34**, 63-75.

(4) Hacker, B.R., Ernst, W.G., and McWilliams, M.O., 1993, Genesis and evolution of a Permian-Jurassic magmatic arc/accretionary wedge, and a reevaluation of the terrane concept in the central Klamath Mountains: Tectonics **12**, 387-409.

(5) Hacker, B.R., and Ernst, W.G., 1993 Jurassic orogeny in the Klamath Mountains: a geochronological analysis: *in* G.C. Dunne and K.A. McDougali (eds.), Mesozoic Paleogeography of the Western United States—II: Soc. Econ. Paleontol. Mineral., Pacific Section **71**, 37-60.

(6) Hacker, B.R., 1993, Evolution of the northern Sierra Nevada metamorphic belt: petrologic, structural, and Ar/Ar constraints: Bull. Geol. Soc. Amer. **105**, 637-656.

(7) Hacker, B.R., and Peacock, S.M., in review, Creation, preservation, and exhumation of ultrahigh pressure metamorphic rocks: *in* Coleman, R.G., and Wang, X. (eds.), Ultrahigh-Pressure Metamorphism, Cambridge Univ. Press.

(8) Hacker, B.R., Donato, M.M., Barnes, C.G., McWilliams, M.O., and Ernst, W.G., in review, Geochronology and orogeny: Jurassic reconstruction of the Klamath Mountains:

(9) Ernst, W.G., in preparation, Areal geology of the Sawyers Bar region, central Klamath Mountains, northern California: scale 1:48,000: Geol. Soc. Amer. Maps and Charts Series.

(10) Hacker, B.R., and Ernst, W.G., in preparation, Lithotectonic terranes and regional metamorphism of the Klamath Mountains, NW California and SW Oregon: scale 1:200,000.

Department of Energy
Washington, DC 20585

JUN 04 1993

Dr. W. G. Ernst
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Dear Dr. Ernst:

You have been hearing from me occasionally on the topic of the OPA Peer Review of our research program and the associated (but independent) workshops. You should also have heard from OPA Representatives at Oak Ridge regarding the proposed schedule and related organizational matters for the July 13-14 OPA review. If you haven't heard from them yet please let me know. So far you haven't heard much about the workshop, thus this letter.

Hal Wollenberg has agreed to host the workshop at Lawrence Berkeley Laboratory and has planned a "field trip" to the Advanced Light Source at LBL. This letter is a **request for submission of abstracts to Hal** and provides you with a point of contact at LBL to facilitate planning for your stay in the Berkeley area. It would be helpful if you would provide Hal with information on your travel and lodging plans as well as your potential interest in the visit to the ALS. By the way, **the workshop is completely independent of the OPA review** and the OPA contacts at Germantown or Oak Ridge have no detailed knowledge of what we plan.

Your ten-page OPA summaries should be satisfactory as a base for the workshop abstracts. You should be able to retain all but items 2, 3, 4 and 5D referenced in pages 43-45 of DOE/ER-0491P. Of course you are free to modify the content in ways that you believe more appropriate for the workshop audience. We plan to have the abstracts bound and available for distribution at the workshop. Your workshop abstract should be sent to Hal, with a copy to me by June 20.

Current Plans are to hold the workshop at LBL, Building 50 Auditorium on July 15th and 16th. Buses will be available from the Claremont to Building 50 in the morning and evening. Hal will send you a provisional agenda and will have an informational packet available at the OPA review preceding the workshop which will contain final details.

A passing note on the OPA review. The reviewers are charged specifically with evaluating how well the issues noted in their manual (page 7 of DOE/ER-0491P) are addressed. In some of the BES reviews so far, the PIs have not fared well in providing information which addresses these questions in a straightforward manner. In particular, reviewers respond negatively when the stated objectives of the research project do not mesh well with the activities underway.

The two previous workshops, in January at Caltech and in April at Sandia, have been quite successful from my point of view and, I believe, from the standpoint of the participants. I look forward to your participation in the July Workshop in Berkeley and will enjoy talking with you again. Thanks very much for your cooperation in getting the information in to OPA and to Hal Wollenberg in a timely fashion.

All the best.

Sincerely,

Bill

William C. Luth, Manager
Geosciences Research Program
Office of Basic Energy Sciences

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Grain Boundary Transport and Related Processes in Fine-Grained Aggregates

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Completed Project Objectives:

We have developed a new technique for measuring grain boundary diffusion rates in polycrystalline aggregates and have successfully employed this technique to determine oxygen (in the form of molecular water) grain boundary diffusion rates in natural fine-grained quartz aggregates (novaculites) over a wide range of temperatures (Farver and Yund, 1990; Farver and Yund, 1991a). In addition, we have demonstrated the major role of fluid composition on the microstructure and oxygen grain boundary diffusion rate in a novaculite sample (Yund and Farver, 1990; Farver and Yund, 1992). Also, we have successfully produced hot-pressed fine-grained monomineralic quartz and feldspar aggregates and have measured oxygen grain boundary diffusion rates in these aggregates for comparison to the natural novaculite samples (Farver and Yund, 1991b). Details of these results follow and the data are summarized on an Arrhenius plot in Fig. 1.

Oxygen Grain Boundary Diffusion in Fine-Grained Quartz Aggregates

Oxygen grain boundary diffusion rates have been measured in two fine-grained quartz aggregates (Arkansas novaculite) with 1.2 and 4.9 μm diameter grains. SEM and TEM observations show that both samples have equilibrium microstructures consisting of equant grains with triple grain junctions that meet at ~120°. In addition, the grain boundaries are very tight with physical widths on the order of ≤10 nm. Samples were annealed hydrothermally at 450° to 800°C and 100 MPa confining pressure using 98% ^{18}O enriched water. Profiles of $^{18}O/(^{18}O+^{16}O)$ with depth from the surface were measured using an ion microprobe. Data are collected from a 68 μm diameter circle centered on a rastered area 150-200 μm on a side. Hole depths are measured using an optical interferometer. By collecting data from an area much larger than the grain size of the sample, diffusion along many individual boundaries is averaged to yield a representative value for grain boundary diffusion in the sample.

Using graphical solutions appropriate to the boundary conditions employed, and knowing the volume diffusion coefficient, the product of the grain boundary diffusion coefficient (D') and effective boundary width (δ) is calculated. The value of D'δ is independent of the grain size,

geometry and grain boundary tortuosity. An Arrhenius plot (Fig. 1a) of the data yields straight lines for both the 1.2 and 4.9 μm grain size samples and the Arrhenius parameters are: $D'_{gb}\delta$ = 2.6 and 3.4 x 10^{-17} m^3/s, and activation energy (Q) = 27 ±1 and 26 ±3 kcal/mol, respectively. The activation energy of both samples, ~27 kcal/mol (113 kJ/mol), is significantly less than that for volume diffusion of oxygen in quartz, but greater than that for ionic diffusion in a static fluid. Measured D'δ values are within the range of values reported from theoretical considerations and field observations as well as experimentally determined lamellar boundary diffusion of oxygen in perthite. Assuming an effective grain boundary width of ~10 nm, the measured oxygen grain boundary diffusion is 3 to 4 orders of magnitude greater than oxygen volume diffusion in quartz and ~5 orders of magnitude less than ionic diffusion in a static fluid over the temperature range of the experiments.

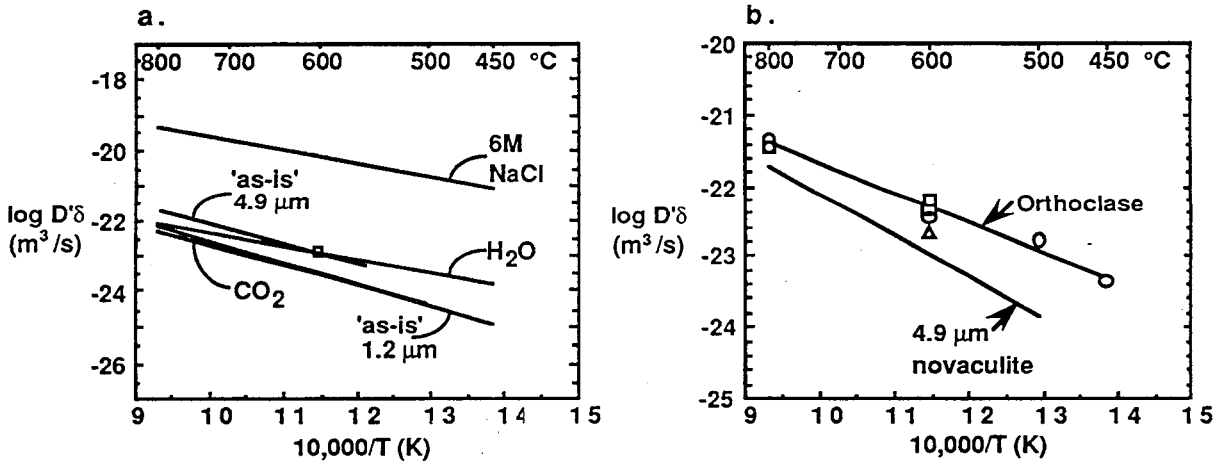

Fig. 1 (a) Arrhenius plot of log D'δ versus reciprocal absolute temperature for oxygen grain boundary diffusion in 1.2 and 4.9 μm grain size novaculite. The straight lines are invariant least squares fits over the temperatures where data were collected. The lines are labelled to indicate the fluid composition that the sample was texturally equilibrated with prior to the diffusion anneal. The 'as-is' lines are from Farver and Yund [1991] and refer to the results of diffusion anneals of samples with their original microstructures. The open square is a sample that was annealed first with 6M NaCl, and then with pure CO_2, to test the reversibility of textural equilibration.

(b) Arrhenius plot for oxygen grain boundary diffusion in hot-pressed feldspar and quartz aggregates. The symbols distinguish different hot-pressed aggregates: squares = albite, circles = orthoclase, and triangle = quartz. The straight lines are invariant least squares fits over the temperatures where data were collected. The orthoclase line is from this study, and the 4.9 μm novaculite line, drawn for reference, is from Farver and Yund [1991].

The Role of Fluid Composition on Microstructure and Oxygen Grain Boundary Transport in Fine-Grained Quartz Aggregates

Oxygen grain boundary diffusion rates have been measured in the 1.2 μm grain size quartz aggregate (Arkansas novaculite) described above, after anneals with wetting and non-wetting fluids, to determine the effect of microstructure on oxygen grain boundary diffusion rates. Samples were annealed at 800°C and 150 MPa confining pressure for 6 to 12 days with pure CO_2, pure H_2O, or H_2O + NaCl (~6M) to produce new equilibrium microstructures. The pure CO_2 and pure water fluids produced non-wetted structures (θ>60°); samples annealed in pure CO_2 showed no changes, and samples annealed in pure water showed minor changes, including the formation of

small pores at many of the triple grain junctions. In contrast, the water + NaCl fluid produced a microstructure ($\theta<60°$) with large pores at essentially all of the triple junctions indicating an interconnected fluid distribution. These microstructures are consistent with the wetting behavior of these fluids for quartz aggregates as reported by other workers (e.g. Watson and Brenan, 1987; Lee et al., 1991).

After the textural equilibration anneals, the samples were annealed at 800° to 450°C and 100 MPa confining pressure with 98% ^{18}O-enriched water to determine the grain boundary diffusion rates. The short duration and lower temperature of the diffusion anneals produced no further changes in the microstructures. Profiles of $^{18}O/(^{18}O+^{16}O)$ with depth from the surface were measured using an ion microprobe, and the product of the grain boundary diffusion coefficient (D') and effective boundary width (δ) determined. As shown in Fig. 1a, compared to the starting material, the D'δ values for samples texturally equilibrated with pure CO_2 and pure water are about the same and about four times greater, respectively. The D'δ values for samples texturally equilibrated with 6M NaCl are three to four orders of magnitude greater than that for the starting material. In addition, the D'δ value for a sample texturally equilibrated first with 6M NaCl and then with pure CO_2 is about a factor of three greater than the value for the starting material, demonstrating that textural equilibration is reversible.

The results of this study indicate that grain boundary transport rates in quartz aggregates are strongly influenced by the microstructure which, in turn, depends on fluid composition. In non-wetted samples, changes in grain boundary structure or the formation of small isolated pores at triple junctions can change D'δ values by changing δ. However, this effect is minor compared to the change in D'δ values for samples with non-wetted versus wetted microstructures. The much faster rates for samples with interconnected fluid distributions are believed due to oxygen transport (probably in the form of molecular water) along the interconnected channels by ionic diffusion in the static fluid. The connected porosity in these samples is <1% of the total porosity, a result which is consistent with estimates from natural contact zones (Nagy and Parmentier, 1982).

Oxygen Grain Boundary Diffusion in Hot-Pressed, Fine-Grained Monomineralic Quartz and Feldspar Aggregates

The above technique that we have used for measuring grain boundary diffusion rates in polycrystalline aggregates requires fine grain size (<10 μm) material to eliminate grain boundary cracking. This constraint greatly limits the availability of natural samples, prompting us to hot-press fine-grained aggregates. We have begun with quartz which can be directly compared to the natural novaculites, and with alkali feldspars which afford the possibility of determining grain boundary diffusion rates for cations as well as oxygen in a geologically important mineral. The quartz aggregates were prepared using sized 1-3 μm diameter fragments of a natural quartz from US Silica (supplied by B. Evans). The albite aggregates were prepared using 2-4 μm sized fragments of a natural albite ($NaAlSi_3O_8$) and the orthoclase aggregates were prepared using 2-4

μm sized particles of 'orthoclase' ($KAlSi_3O_8$) glass from Corning (supplied by R. Cooper). All of the samples were vacuum dried at 250°C before hot-pressing at 900° (Qtz), 1060° (Ab) or 1100°C (Or) and 1.5 GPa, for 5 hours (Qtz) or 20-24 hours (Ab and Or). Grain-scale cracking was essentially eliminated by packing the sealed samples in NaCl and cooling at 3°C/minute along with slow decompression. TEM examination of the quartz aggregate indicates a microstructure similar to the novaculites with some porosity (<1%) located at three-grain junctions. The albite aggregate has some porosity (<1%) because the lath-shaped fragments do not pack well, but most grain boundaries are 'tight' (<10 nm). The orthoclase glass crystallizes to form an equilibrium texture with a very low porosity (near zero) and tight grain boundaries. Use of a fine particle size for devitrification of the Or glass is critical to produce an equilibrium rather than a spherulitic texture (R. Cooper, pers. comm.).

The product of the oxygen grain boundary diffusion coefficient (D') and the effective grain boundary width (δ) has been determined for these aggregates and the data are plotted in Fig. 1b. The D'δ values for the Or and the Ab aggregates are similar, and at 600°C are approximately a factor of four greater than that for a 4.9 μm novaculite and nearly equal to oxygen diffusion along macroperthite lamellae (Nagy and Giletti, 1985). The similarity between the D'δ values obtained for the two different feldspar aggregates indicates that the small amount of porosity remaining in the albite aggregate has no measurable influence on the oxygen grain boundary diffusion rates. This is consistent with our previous observations for quartz aggregates which indicated that it is not simply the presence, but rather the interconnectedness, of the porosity that influences the grain boundary transport rates in fine-grained aggregates. The activation energies for the feldspar aggregates, ~18 kcal/mole, are less than that for the 4.9 μm novaculite (26 kcal/mole), and much less than that for macroperthite lamellar boundaries (43 kcal/mole). The results of this study indicate that these hot-pressed aggregates can provide suitable material for grain boundary diffusion determinations of oxygen, and that the feldspar aggregates should be suitable for cation determinations as well.

Current Project Objectives:

Grain Boundary Diffusion in Feldspar Aggregates

Oxygen grain boundary diffusion rates have been determined in a series of monomineralic feldspar aggregates. These include a natural albite composition rock from the Tanco pegmatite, an aggregate prepared by hot-pressing 2-4 μm sized fragments of a natural albite sample (Amelia Albite), and aggregates prepared by hot-pressing synthetic albite ($NaAlSi_3O_8$), orthoclase ($KAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$) composition glasses from Corning (supplied by R. Cooper). The results indicate that oxygen grain boundary diffusion rates are very similar over the wide range of feldspar compositions employed and that the hot-pressed aggregates provide very good analogs to natural feldspar samples for determining grain boundary diffusion.

The success in measuring oxygen grain boundary diffusion rates in these feldspar samples has allowed us to expand this work to include determining grain boundary diffusion rates for select geologically and environmentally important cations. We have begun by determining potassium and calcium grain boundary diffusion rates in hot-pressed orthoclase and anorthite aggregates, respectively. In addition to knowledge of their own behavior, these two elements should provide valuable insights into the behavior of other alkali (*ie* Rb, Cs) and alkaline earth (*ie* Sr and Ba) cations.

The grain boundary diffusion rate for potassium in an orthoclase aggregate has been determined both under hydrothermal and anhydrous conditions. The results indicate that there is no difference in the potassium grain boundary diffusion rate when water is present. However, D'δ values for potassium are different from values for oxygen even in those experiments where diffusion profiles of both elements were measured. The ability to measure D'δ values for different chemical species in the same experiment provides clear evidence that the transport process being measured is diffusion. As stated above, we have also measured calcium grain boundary diffusion rates in anorthite aggregates. The results indicate that calcium grain boundary diffusion is several orders of magnitude slower than oxygen in anorthite, and also, is orders of magnitude slower than potassium in orthoclase. This suggests that differences in size and formal charge of chemical species may play an important role in their relative grain boundary diffusion rates.

Grain Boundary Diffusion in Calcite Aggregates

The technique that we have employed to determine grain boundary diffusion rates requires knowledge of the volume diffusion rates of the chemical species of interest in the material of interest. Published values of oxygen and carbon volume diffusion rates in calcite are available, however, no data exit for calcium. Hence, to allow us to determine calcium grain boundary diffusion rates in calcite aggregates we have first done a series of experiments to measure calcium volume diffusion rates in calcite single crystals.

In addition to determining the calcium volume diffusion rates in calcite, we have begun to evaluate the suitability of various natural and hot-pressed calcite aggregates for grain boundary diffusion studies. Preliminary results using Solenhofen limestone (which was texturally equilibrated prior to the diffusion anneals) indicate that although microcrack formation due to the anisotropy of thermal expansion of individual grains is extensive, the healing rate may be fast enough that the grain boundary diffusion profiles are not significantly affected by the microcracking.

Equilibrium Fluid Distributions in Feldspar Aggregates

A series of experiments has been initiated to determine the equilibrium distribution of geologically common fluids in feldspar aggregates. Samples of hot-pressed aggregates of natural Amelia albite and of synthetic albite and orthoclase composition have been texturally equilibrated with water and dilute NaCl solutions at a variety of temperatures, durations, and heating and

cooling rates. The sample microstructures have been characterized using transmission electron microscopy. Results to date suggest that the equilibrium distribution of water in feldspar aggregates is that of unconnected isolated pockets. Studies continue in order to evaluate the role of pressure and non-hydrostatic stresses on fluid/feldspar interfacial energies.

Future Project Objectives:

The future objectives include completion of the experimental determinations of grain boundary diffusion rates of cations in feldspar aggregates. In addition, we will characterize (using TEM and SEM) calcite aggregates to identify appropriate starting materials. These samples will include both natural and hot-pressed calcite aggregates. After identifying appropriate starting materials, we will experimentally determine grain boundary diffusion rates for oxygen and calcium in calcite aggregates.

A significant portion of our future efforts will be devoted to characterizing the fluid distribution in feldspar composition aggregates as a function of fluid composition, pressure and hydrostatic versus non-hydrostatic stresses. These studies will then be expanded to include geological more common samples with polymineralic compositions. We will begin with bimineralic quartz and feldspar aggregates which will be characterized using TEM and SEM observations and then used for bulk diffusion studies.

ABSTRACT

Project title	Geochemical Incorporation of Sulfur into Organic Matter: Role of Sulfur in the Formation and Diagenesis of Macromolecular Organic Matter in Sediments
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The World's potential reserves of heavy oils and tar sands (generally high in sulfur content) greatly exceed known reserves of conventionally produced low-to-moderate sulfur petroleums. Increasing use of these potential resources must be realized unless alternative energy sources replace fossil fuels. The chemistry of sulfur in fossil fuels is thus of both practical (economic) and academic interest. The behavior of sulfur during the processing of high sulfur fossil fuels (crude oils, coals and natural gas) to make environmentally acceptable products poses special engineering problems and economic penalties, and the success of methods to reduce sulfur prior to, and during fossil fuel processing, are dependent upon the molecular structure and form of organically-bound sulfur. Since the sulfur content of oil is determined primarily by the sulfur content of the source rock kerogen, understanding the geochemistry of the latter is of fundamental importance. Moreover, various investigators have proposed that high sulfur kerogens start to generate petroleum at thermal exposures significantly lower than classical oil-prone kerogens. Likely key factors controlling the kinetics include not only total sulfur content, but also the structures of the sulfur-containing functional groups in kerogen. In spite of its importance, little is known about the amount and forms of sulfur in most kerogens although it is thought to be present as sulfide, disulfide and heterocyclic moieties. The very high $S_{organic}/C$ ratios (0.04-0.09) of some kerogens imply an important role for sulfur in the kerogen macromolecular network. Attempts to accomodate this amount of sulfur into a kerogen model is difficult without invoking significant amounts of disulfide or polysulfide moieties or a large number of sulfur cross-linkages.

Our investigations are thus concerned with (1) how and when sulfur is introduced into the natural biogenic materials which are the precursors of fossil fuels, (2) why and how the abundance and forms of sulfur differ in various geologic environments and (3) how abundance and forms of sulfur evolve with subsequent maturation. The major source of organically-bound sulfur in sedimentary kerogens and petroleums is H_2S (and other reduced sulfur species) derived from dissimilatory sulfate reduction. In surficial sediments containing limited amounts of reactive iron, reduced sulfur species are available for reaction with organic matter. Functionalized lipids are thought to be the major targets for sulfur attack and, depending on their structure (# and position of functional groups), sulfur may react in an intra- or inter-molecular fashion. The latter mechanism is believed to give rise to the formation of sulfur cross-linked macromolecules precursing kerogen. It has even been suggested that the degree of sulfur-crosslinking may control the molecular-size distribution in sulfur-rich organic matter. It has been hypothesized that macromolecularly-bound sulfur can be represented by one (or more) of four different basic model structures. These structures differ in the sulfur linkage type (inter-molecular bridges vs intra-molecular bonds), as well as the number of linkages per molecule and the number of sulfur atoms in each linkage (i.e. mono- vs di- or poly-sulfide). Our intention is to test these models through determination of the types, positions and numbers of sulfur linkages as well as the structural features (carbon skeletons) of the molecules containing sulfur. This information is used to address two specific issues: (a) the significance of sulfur as an agent promoting kerogen formation in sediments (through abiotic cross-linking reactions) with respect to the occurrence of organic-rich petroleum source rocks and (b) the role of sulfur in "early" petroleum generation.

A multifaceted analytical approach has been adopted in order address these issues. X-Ray absorption spectroscopy (XANES) is used for determination of sulfur speciation and specifically to quantitatively distinguish organic sulfides, thiophenes and sulfoxides. Chemical degradation experiments are employed to selectively cleave organic molecules linked by sulfur, providing information on linkage type (i.e. di- or polysulfide *vs.* monosulfide), the sites of sulfur attachment, the number of linkages involved and the molecular structures of the sulfur-containing molecules; analytical pyrolysis is used to derive structural information and to provide estimates on organic sulfur content. These analyses are performed in addition to conventional bulk measurements (elemental analysis, TOC etc.) on a series of fractions isolated from sedimentary organic matter according to approximate molecular size (gel permeation chromatography) and/or solubility. In this way information is derived for each molecular size range, concerning the organic sulfur content, the type of organic molecules involved (*i.e.* chain-length, carbon skeleton), and the type (acyclic *vs* cyclic, mono *vs* di or polysulfide *etc.*) and number of sulfur bridges per organic molecule. Models constructed based on, and constrained by, these results are assessed by comparison of samples of varying type (molecular size, depositional environment, diagenetic stage *etc.*).

The Peru margin was selected as the primary study area because of its high sedimentary organic carbon and organic sulfur contents (C_{org} ≈ 10%; $S_{org.}$ up to 10%), and because of the perception of these sediments as a modern immature analogue of Monterey Formation and other sulfur-rich source rocks. The Peru samples selected for initial study were obtained from a shallow (<1 meter) box core and a 100 m ODP core from the center of the oxygen minimum zone. The PI participated in a scientific cruise to the Peru margin last fall and fresh surface sediment samples were collected specifically for organic sulfur geochemical investigation. These cores were obtained from two transects across the shelf (at 12°S and 13°S) and cover a range of organic contents (mainly as a function of location relative to the oxygen minimum zone). In addition to the Peru and Monterey Fm sediments targeted for detailed investigation, selected samples were studied from the Kimmeridge, Jurf ed Darawish, Serpiano, Phosphoria and New Albany shales varying in terms of depositional conditions, source input and maturity.

Mineral-free solvent extracts (bitumen fractions) have been isolated from Peru and Monterey Fm sediments and elemental composition and sulfur speciation in these samples has been determined. Each extract was analyzed by Gel Permeation Chromatography (GPC) in order to provide information about its molecular size distribution. Kerogen samples and soluble high molecular weight fractions (see below) are analyzed by flash pyrolysis-gas chromatography in combination with either a sulfur selective detector (Py-GC-FPD) or a mass spectrometer (Py-GC-MS). Solvent extracts from two samples (a shallow Peru sediment and an immature Monterey shale) were separated using preparative GPC into molecular size ranges (up to ca. 20,000 daltons) in order to study variations in sulfur content and speciation. The molecular size fractions are characterized using XANES, analytical pyrolysis and chemical degradation.

Total sedimentary sulfur contents increased from 0.88% to 1.92% across the depth interval studied (*ca.* 100m) in the Peru samples. Elemental analysis of bitumens isolated from the sediments revealed an increase in atomic $S_{org.}/C$ ratio from 0.006 to 0.025. These data confirm previous findings that sulfur incorporation is an early diagenetic phenomenon with the majority of organically-bound sulfur forming in the upper few meters of sediment. XANES analyses of both total sediment and bitumen revealed that most of the organically-bound sulfur in these sediments is present as organic sulfides. In contrast to Peru margin sediments, XANES analyses of sediments and bitumens from consolidated sediments reveal that thiophenic sulfur equals or exceeds the concentration of organic sulfides. These observations are in agreement with the prevailing concepts of aromatization of cyclic sulfides during diagenesis and maturation. Comparison of kerogen/asphaltene or whole rock/bitumen pairs from the same samples revealed a lower thiophene/sulfide ratio for the insoluble organic matter fraction than the corresponding soluble fractions (bitumen or asphaltenes), consistent with a higher degree of sulfide cross-linking in the kerogen. XANES analyses of molecular size fractions isolated from the Monterey shale sample revealed a distinct trend with the percentage of sulfide sulfur increasing with increasing molecular size. This relationship is consistent with the concept of the role sulfide bridges as

determinants on molecular size. No such trend was apparent in the Peru size sample suite, suggesting this relationship has little importance that the very earliest stages of diagenesis.

Our investigations have revealed that the greatest amount of error related to quantitation of sulfur species by XANES spectrocopy is associated with assessment of compounds with -2 oxidation state (sulfides). Potential errors arise because of overlap between inorganic and organic sulfide peaks and also because the strength of the K-absorption edge is much weaker than for more oxidized species. We are currently pursuing several lines of investigation to overcome these uncertainties. First, improvements in the peak deconvolution software are being attempted. Second, we are including new authentic standards as calibration standards (prior to this time, the standards that were employed were those established for assessment of sulfur speciation in coals). Third, we are comparing organic matter fractions both free and associated with their mineral matrices in order assess potential interference by inorganic sulfur compounds. Another relatively early result of the XANES analyses was the observation of a significant percentage of sulfoxides in certain samples and molecular weight fractions. The origin of these compounds is uncertain, but they are in part believed to be oxidation products, related either to weathering or sample processing and storage. Reduction experiments using $LiAlH_4$ are currently being performed to shed light on their precursor molecules. We are also currently assessing the utility of analytical pyrolysis as an independent method of determining the relative abundance of sulfide/thiophene sulfur, and also the amount of sulfide bound in heterocycles relative to that in heterocyclic bridges.

TRACERS IN GEOLOGICAL RESERVOIRS
(Injected and Natural, An Application to Northwest Yellowstone)

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Chemical compositions of springs, seeps, rivers and wells provide significant indications of solution sources, reaction processes and mixing in underground aquifers and reservoirs. Often, however, combinations of multiple natural processes makes interpretation of such information complex and uncertain. In situations where sinks and/or wells are available, injected tracer experiments can provide significant insight. Interpretation of injected tracer experiments are not necessarily unique either, subject to similar limitations as natural compositional information. Combination of multicomponent injected tracer experiments with examination of multicomponent natural compositional variations can provide enhanced and even diagnostic information, with only small increments in effort through the application of modern analytical tools. The Mammoth hydrothermal system provided an ideal area to demonstrate this approach due to previous efforts, relatively short transit times from lower terrace sink holes to Gardner River outflows, and a series of open questions with respect to the hydrologic and geochemical operation of the system locally and regionally.

INVESTIGATION OF ACTIVE AND ANCIENT GEOTHERMAL CONTROLS ON OIL-RESERVOIR EVOLUTION IN THE BASIN AND RANGE PROVINCE OF EASTERN NEVADA

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INTRODUCTION

The Basin and Range physiographic province of northeastern and east-central Nevada is famous not only for the State's eleven productive oil reservoirs (Fig. 1), but also for its dense concentration of Carlin-type, sediment-hosted, disseminated precious-metal deposits. Results of our OBES-sponsored research-in-progress in the region have begun to reveal distinct parallels between these seemingly disparate occurrences. Many of the oil reservoirs are hot, and actually appear to have formed in moderate temperature hydrothermal systems. Several of the clearly paleohydrothermal Carlin-type deposits (like Yankee; Fig. 1) contain considerable liquid hydrocarbon, and may have evolved under physical/chemical conditions quite similar to those presently prevailing at the thermally active oil fields. Our research encompasses both types of occurrences, and is aimed at testing the following general hypothesis: Convecting, moderate-temperature hydrothermal systems in this province have fostered and in some cases have critically influenced the generation, migration, and entrapment of oil.

GEOTHERMAL INFLUENCES IN OIL-RESERVOIR EVOLUTION IN RAILROAD VALLEY

Our research to date has focused on the thermally active oil fields at Grant Canyon and Bacon Flat in eastern Nevada's Railroad Valley (Fig. 1). Grant Canyon has produced nearly 19,000,000 barrels of oil to date since its discovery in 1983, making it the State's premier oil field (Montgomery, 1988; Nevada Department of Minerals bi-monthly production statistics). The adjacent Bacon Flat field produced about 340,000 barrels of oil before being shut in in 1987 (Montgomery, 1988), then was rejuvenated in 1992 by a successful step-out well; the field had produced about 400,000 barrels of oil as of March 1993. A 1993 Cenex Corporation discovery, Sans Spring field (Fig. 1) about 4 miles west of Bacon Flat, has produced as much as 1200 barrels of oil per day (Nevada Department of Minerals).

Both Grant Canyon and Bacon Flat fields, hosted by Devonian dolostone breccias beneath a Plio-Pleistocene valley-fill alluvial sequence, have long been recognized as thermally anomalous (Bortz, 1989; Veal et al., 1988; Read and Zogg, 1988; Duey, 1983) -- Bacon Flat reservoir temperature is probably between 125 and 135°C; Grant Canyon about 121°C (Fig. 2; Hulen et al., 1993a; Veal et al., 1988), corresponding to a simple geothermal gradient (thermal conductivity assumed constant) of about 90°C/km. This value is about three times the global norm (Kruger and Otte, 1973), and more than four times the value cited by Duey (1983) as typical for Railroad Valley overall. Only one published equilibrium-temperature log exists for wells in the two fields (Fig. 2), so our concept of the modern subsurface thermal regime is based upon drill-stem-test (DST) measurements -- these closely match the actual measured temperatures (±10°C) at the same depths in two wells recently temperature-logged by the USGS (C. Williams, USGS, pers. comm., 1993).

Note that the DST temperatures for the two fields and immediate vicinity vary little regardless of depth over an interval of nearly 800 m (a DST temperature for a dry hole four miles north is shown for comparison). We contend that this profile reflects an isothermally upwelling geothermal plume -- one which, moreover, critically influenced oil-reservoir evolution. Above the plume, as signalled by the 4-GC temperature log, a conductive thermal regime corresponds to the fields' effective caprocks.

Modern reservoir waters coexisting with oil at Grant Canyon and Bacon Flat are dilute, meteoric, Na-HCO_3-Cl fluids reminiscent of those circulating in many well-studied, moderate-temperature geothermal systems -- they are, for example, enriched in SiO_2, B, Br, Li, Cs, and Rb (Goff et al., 1993; Hulen et al., 1993a). They do not, however, display a significant "oxygen-shift", or enrichment in del^{18}O relative to modern or older (based on tritium analyses) cool meteoric fluids sampled from springs, shallow wells, and a creek in Railroad Valley and its foothills (Fig. 3). Mathematical modeling of the reservoir waters' exceedingly low tritium content (<1 T.U.; Goff et al., 1993) suggests that they were recharged in pre-Holocene time (>10,000 yr. ago). An array of chemical and isotopic geothermometers (e.g. chalcedony, Na-K-Ca with Mg correction; Fournier, 1981) suggest that the reservoir waters may never have been much hotter than the modern measured temperature range.

The Grant Canyon and Bacon Flat oil-field waters have a measured concentration (4500 ppm total dissolved solids; Goff et al., 1993) virtually identical to the apparent salinity (0.35-0.53 wt.% NaCl equiv.) of primary aqueous fluid inclusions co-existing with oil inclusions in late-stage secondary quartz at both fields. Homogenization temperatures of these inclusions are close to modern reservoir temperatures (Fig. 4) -- for the aqueous inclusions virtually identical when an appropriate, slight pressure correction (Potter, 1977) corresponding to contemporary reservoir pressure is added (Hulen et al., 1993a). The T_h values are the same regardless of elevation at reservoir depths or below -- duplicating the modern-day isothermal profile defined by DST temperatures. Finally, the oxygen-isotopic composition of the quartz (del^{18}O = 5.24 $^o/_{oo}$) is consistent with its precipitation from modern oil-reservoir waters at present-day temperature (Hulen et al., 1993a). These relationships strongly suggest that oil was transported to the Grant Canyon and Bacon Flat traps in an isothermally upwelling plume of dilute geothermal water much like the one apparently still in existence.

The oil-bearing quartz discussed above occurs not only abundantly in the Grant Canyon and Bacon Flat oil reservoirs, but also sparingly in the overlying caprocks, where along with chalcedony, calcite, and kaolin, it helps provide an effective reservoir seal. In view of the quartz-hosted fluid-inclusion systematics summarized above, this suggests that formation of the oil reservoirs did not commence until Railroad Valley was filled with alluvial and lacustrine sediments to essentially modern levels. The fields would appear to be very young features indeed. This contention is supported by consideration of age-dated durations for many active and fossil geothermal systems (e.g. White, 1979; Silberman, 1983; Browne, 1984): few persist longer than 1 m.y., and the oldest dated system, Steamboat Springs, has been intermittently active for only 3 m.y. (White, 1979).

In summary, converging evidence from fluid-inclusion, hydrogeochemical, isotopic, and hydrothermal-alteration studies strongly indicates that the Grant Canyon and Bacon Flat oil reservoirs developed in the geologically recent past in a still-active, moderate-temperature, meteoric-hydrothermal system (Fig. 5). The system created critical secondary porosity through hydrothermal carbonate-dissolution, helped seal reservoir margins by depositing secondary silica, kaolin, and other hydrothermal phases, transported oil to the structural traps, and possibly helped generate oil from otherwise submature source rocks by significantly increasing the local thermal budget relative to the regional norm.

THE OIL-RICH PRECIOUS-METAL DEPOSITS OF THE ALLIGATOR RIDGE MINING DISTRICT

Possible paleohydrothermal analogues of the oil-bearing Grant Canyon/Bacon Flat geothermal systems have been exposed by open-pit mining in the Alligator Ridge mining district, about midway between the oil-field clusters of Railroad and Pine Valleys (including Blackburn field) in eastern Nevada (Fig. 1). Like the oil fields, the Alligator Ridge district occurs in the Nevada oil "fairway", within which potential Paleozoic source rocks are regionally "trembling on the brink" of oil generation (Poole et al., 1983; Bortz, 1983). Three Carlin-type, sediment-hosted precious-metal deposits in the district -- Casino, Winrock, and Yankee (Fig. 1) -- contain considerable quantities of oil, either freely flowing as at Yankee (Hulen et al., 1993; Pinnell et al., 1991) or as abundant, oil-rich fluid inclusions, found at all three deposits. The Carlin-type deposits as a class all contain hydrocarbons (e.g. Ballantyne, 1988), and numerous workers (e.g. Nelson, 1991) have suggested that many of these orebodies actually formed in pre-existing petroleum reservoirs. However, in most of the Carlin-type deposits, the hydrocarbons are "burned-out", that is, tarry or asphaltic residues. By contrast, the hydrocarbons in the three above-mentioned deposits are dominantly "live", theoretically once-producible oil, apparently transported and entrapped at unusually low temperatures for epigenetic ore deposits. Results of our work to date at Alligator Ridge strongly suggest that here the oils were transported and entrapped in moderate-temperature hydrothermal systems remarkably similar to those still circulating at the nearby Grant Canyon, Bacon Flat, and Blackburn fields.

The gold ores of the Alligator Ridge district are hosted by Paleozoic carbonate and carbonate-rich siliciclastic rocks. In the high-grade centers of the deposits, these have been massively decalcified, silicified, and sulfidized (e.g. Hulen et al., 1993b; Ilchik, 1991). Partially encircling the orebodies are gold- and arsenic-rich calcite-vein stockworks, within which the calcites have isotopic signatures distinctly different than post-ore varieties (Fig. 6). At the Yankee mine, the calcite-stockwork zone (where unoxidized) hosts conspicuous and abundant concentrations of freely-flowing oil -- and the calcite itself contains large, abundant, primary oil-bearing fluid inclusions trapped at unusually low temperatures.

Figure 7 (from Hulen et al., 1993b) portrays fluid-inclusion T_h systematics for oil-bearing and coexisting aqueous fluid inclusions in the ore-stage Yankee calcites. Note that none homogenize above 150°C, and that the oil-bearing varieties have a mean T_h of about 95°C -- even though the host calcites were collected less than 10 m from >0.05 oz/T gold ore. T_h here is believed on textural and stratigraphic evidence to approximate closely actual entrapment temperatures. We conclude that at Yankee, oil was transported and entrapped in the same hydrothermal system responsible for gold mineralization, and moreover at temperatures far lower than typical for the Carlin-type deposits (190-250°C; e.g. Percival et al., 1988).

The Yankee mineralization temperature, however, is very similar to both the modern reservoir temperature and to that recorded by late-stage fluid-inclusion T_h at the Grant Canyon and Bacon Flat oil fields. Other similarities between the two types of occurrences, besides the obvious presence of oil, include: porosity formation by massive carbonate dissolution; a distinctive trace-element suite including As, Sb, Hg, and Au (only traces of the latter, however, at Grant Canyon/Bacon Flat), and a centrally-located alteration/mineralization assemblage of quartz-kaolin-barite-pyrite/marcasite. In combination, these similarities warrant the working hypothesis that the thermally active Nevada oil fields represent either weakly mineralized analogues of the Alligator Ridge paleo-systems, or possibly an incipient phase in their evolution. The corollary to this suggestion is that within the Nevada oil fairway, deeper, unoxidized, "Carlin-type" oil reservoirs may be found in the future.

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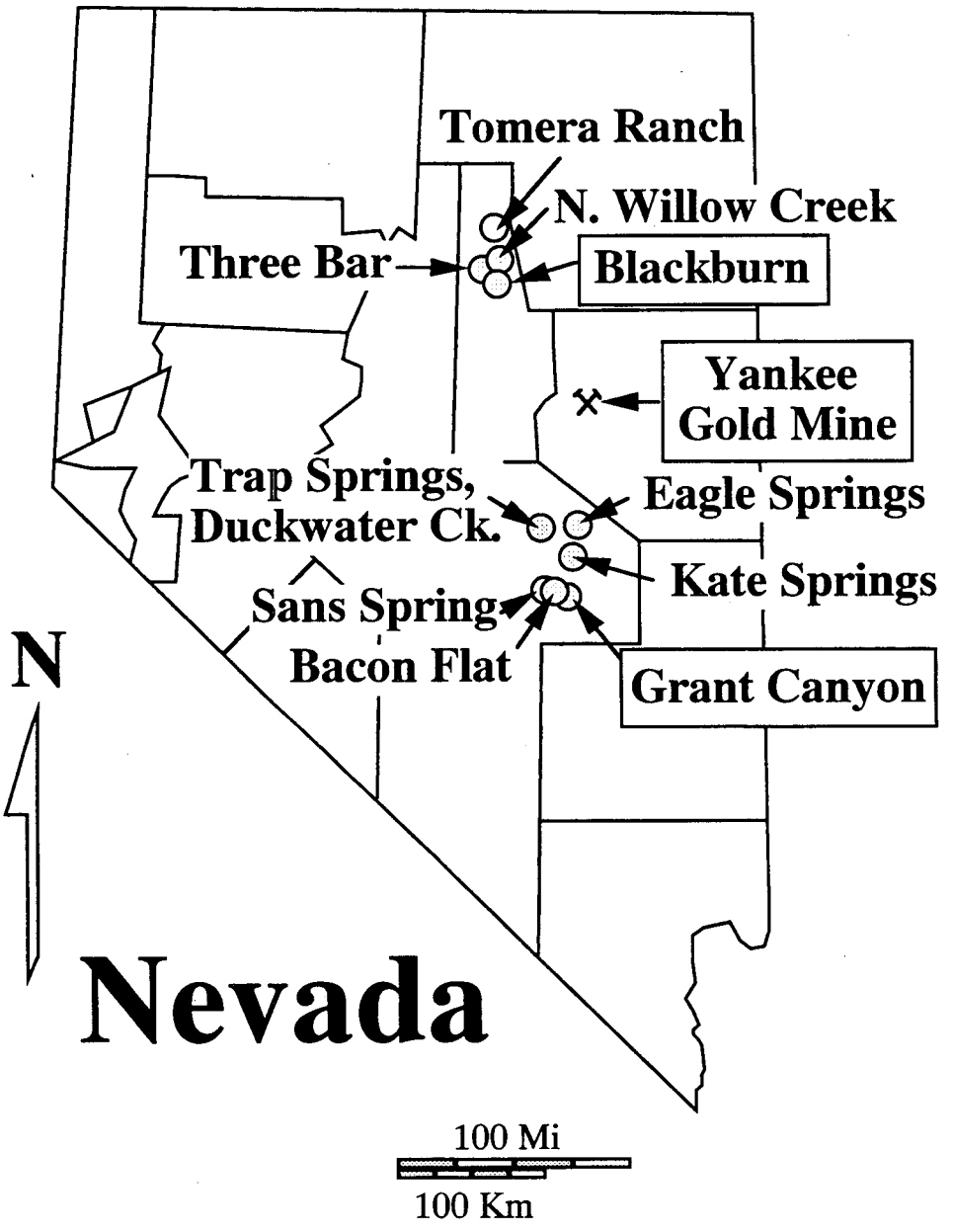
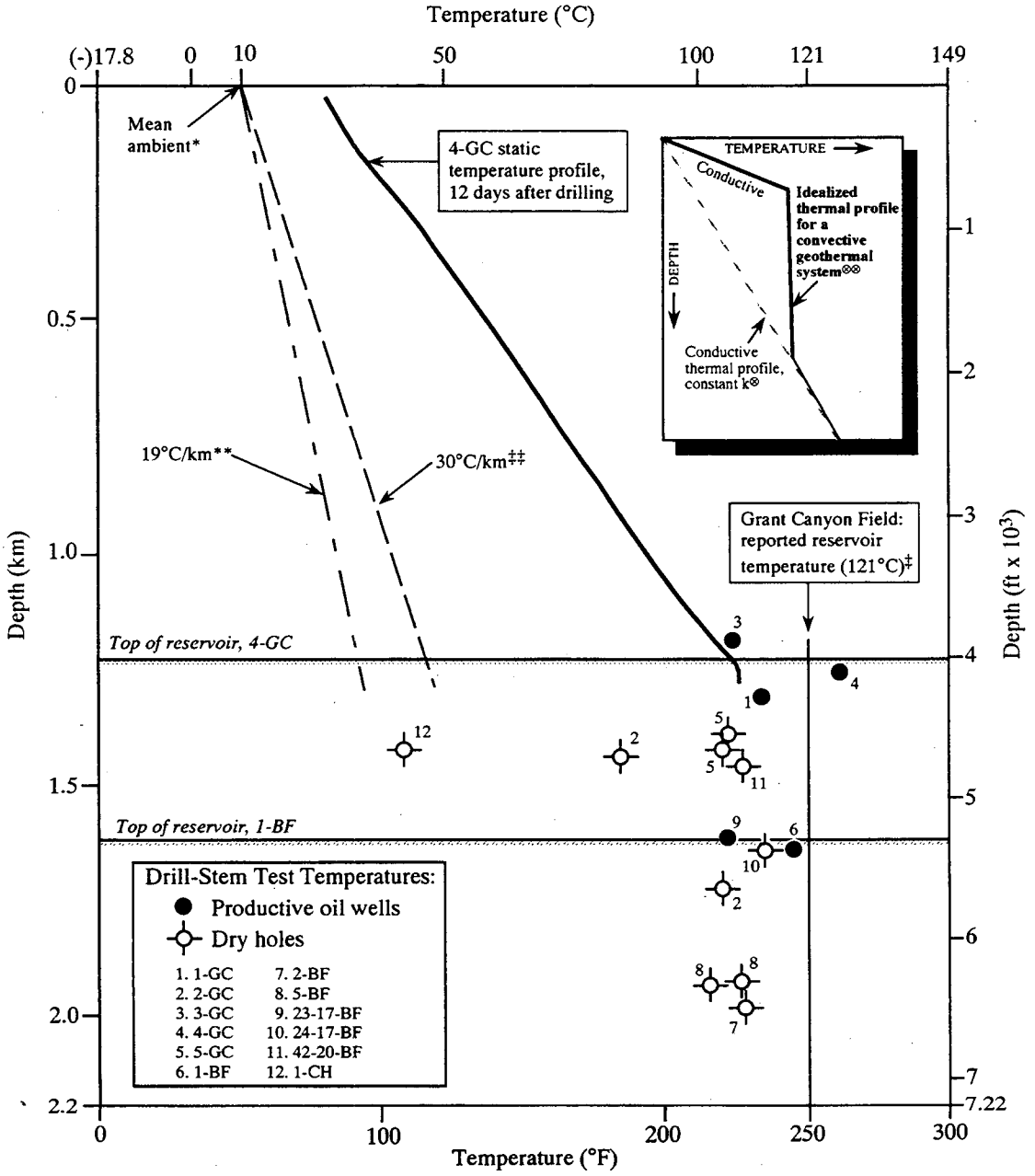


Figure 1. Location map, showing productive oil fields of Nevada and the Yankee gold mine in the Alligator Ridge mining district.



• Kleinhampl and Ziony (1985)
‡ Veal et al., 1988
** Typical Railroad Valley geothermal gradient reported by Duey, 1983
‡‡ Approximate global "normal" geothermal gradient (Kruger and Otte, 1973)

⊗k = Thermal conductivity
⊗⊗Moderate temperature, non-boiling

Figure 2. Composite temperature vs depth profile for Grant Canyon and Bacon Flat oil fields and vicinity, Railroad Valley, Nevada. The profile is formed by linking a static-temperature log for well 4-GC with the locus of temperatures measured during drill-stem tests (DST) of five productive and six non-productive oil wells. Shown for reference, and underscoring the heat anomaly at the oil fields, are typical geothermal gradients for Railroad Valley (Duey, 1983) and the world (Kruger and Otte, 1973), as well as a DST temperature at comparable depth for nearby dry hole 1-CH. Note that the composite thermal profile for the two oil fields closely matches that theoretically predicted for a convectively-upwelling, moderate-temperature geothermal plume beneath a conductively heated caprock (inset). Such a plume, we contend, was instrumental here in oil-reservoir evolution.

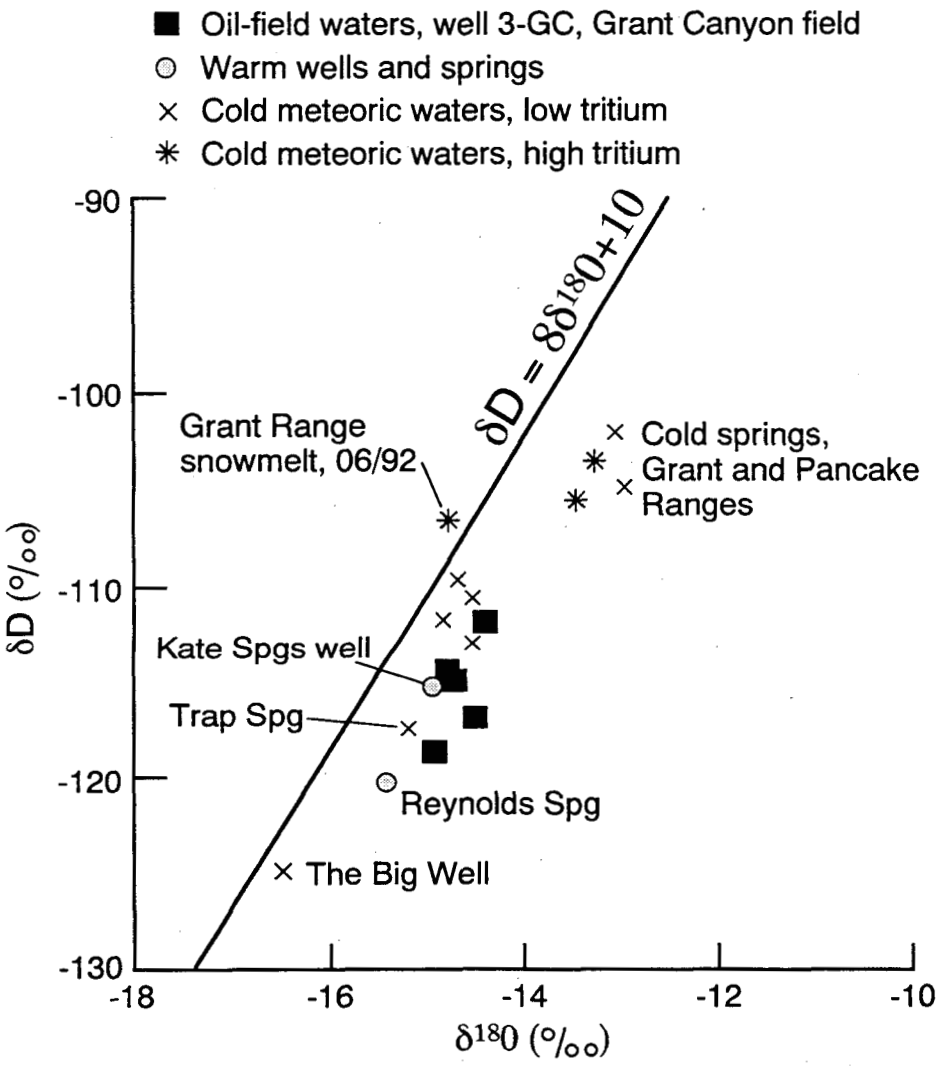


Figure 3. Plot of del^{18}O vs del-D for thermal oil-field waters from Grant Canyon oil field vs other thermal and non-thermal waters collected from Railroad Valley and flanking mountain ranges. Note that the the Grant Canyon oil-field waters are considerably depleted in both isotopes relative to cold meteoric waters from the ranges, ruling out reservoir recharge from modern precipitation. Note also that the the oil-field waters have not become significantly enriched in del^{18}O with respect to the cooler meteoric waters, and thus have apparently interacted minimally with the rocks through which they have circulated.

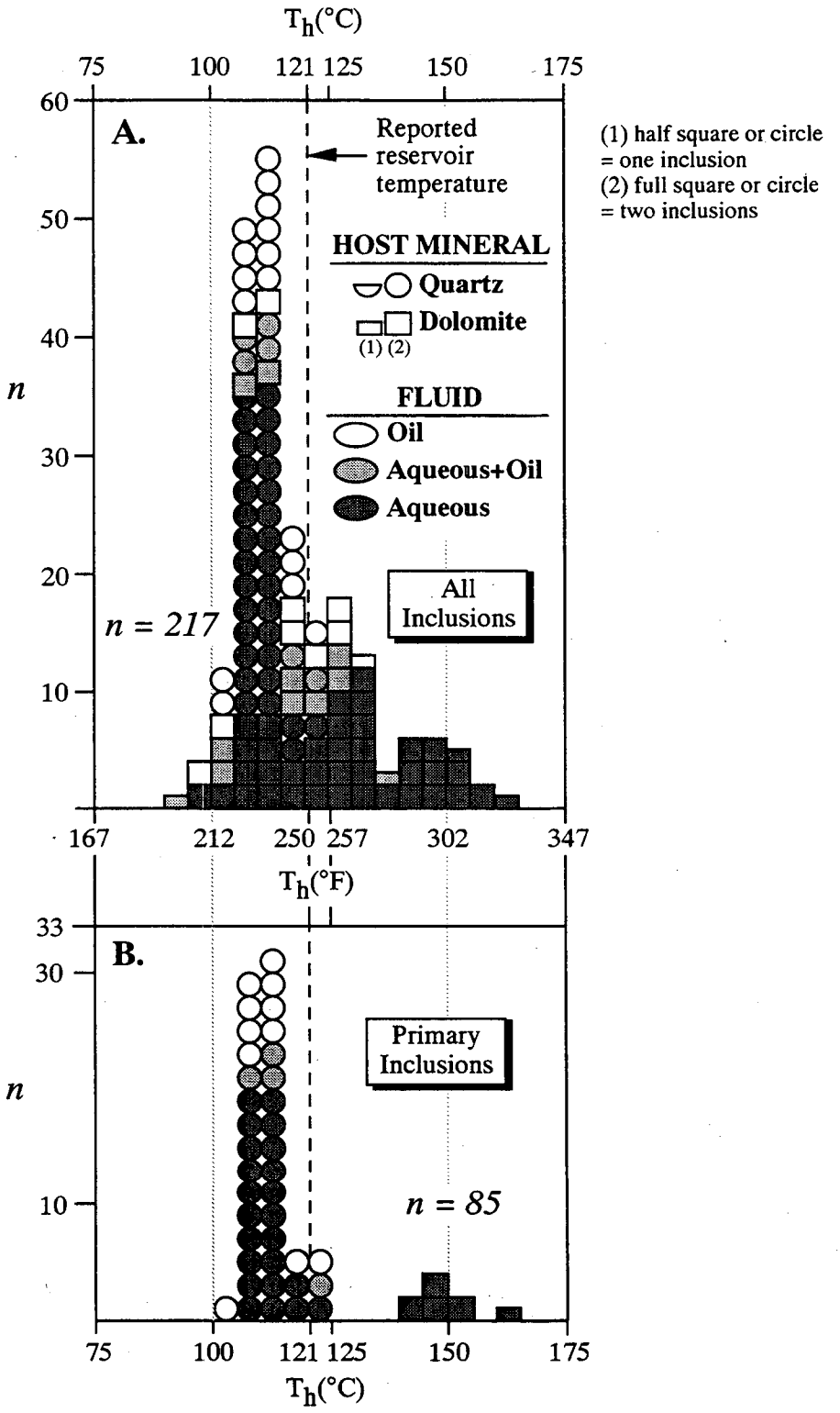


Figure 4. Plots of homogenization temperatures (T_h) vs frequency for aqueous and oil-bearing fluid inclusions in cores and cuttings spanning the elevation interval 80.8-331.9 m in productive wells 1-GC, 4-GC, and 7-GC at reservoir depths in Grant Canyon oil field. T_h data for these wells are similar regardless of elevation and are grouped here for clarity. **A** -- Plot for all inclusions analyzed, showing a prominent T_h maximum in the range 110-115°C. **B** -- Plot for unambiguous primary inclusions only. Two populations are apparent on this plot. One population corresponds to the T_h maximum observed in A, and includes only quartz-hosted primary oil, aqueous, and mixed oil/aqueous inclusions; the other corresponds exclusively with "saddle" dolomite-hosted, primary brine inclusions. Note that the lower T_h maximum is very close to the modern measured reservoir temperature of about 121°C.

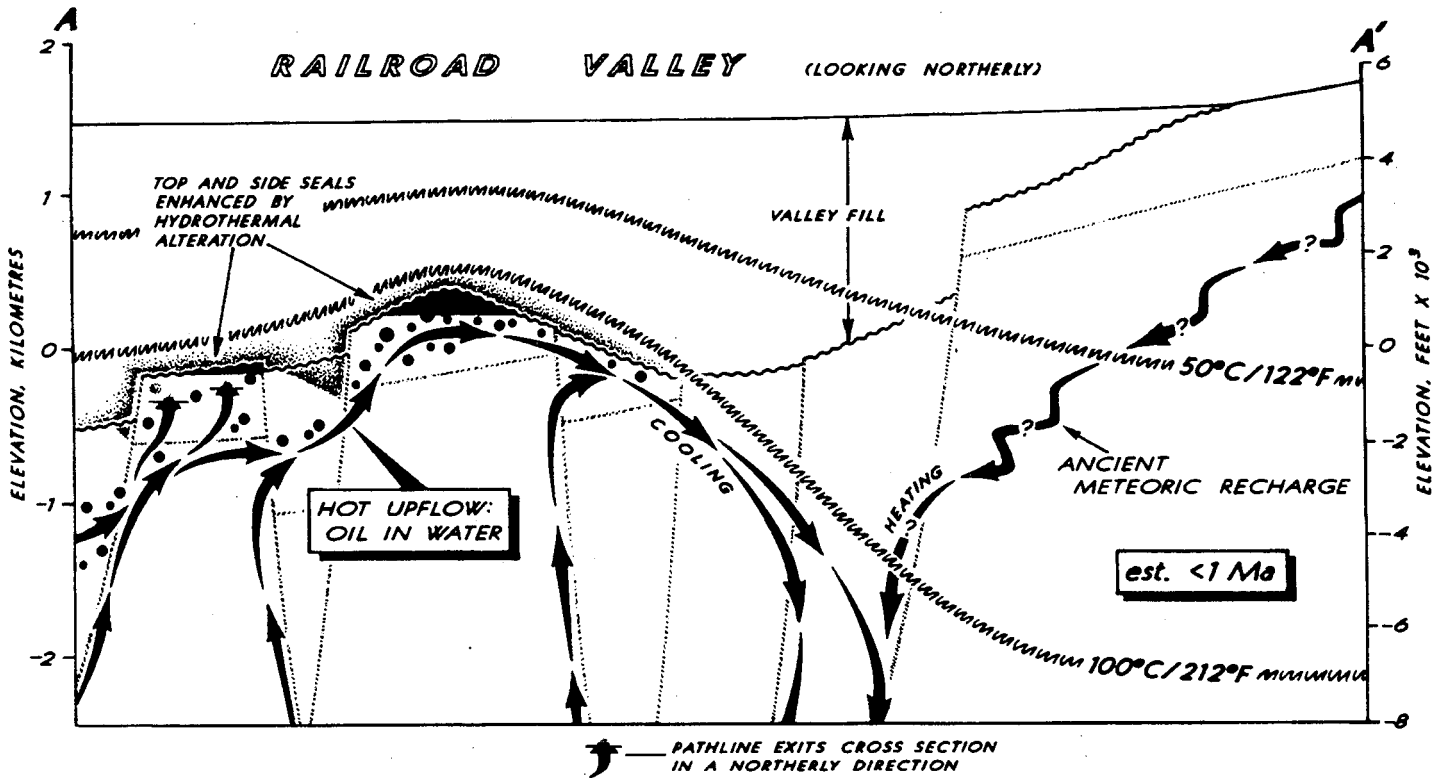


Figure 5. Conceptual model for geothermal evolution of the Grant Canyon and Bacon Flat oil fields. The key element of the model is a convectively upwelling, moderate-temperature plume, which heats the rocks at modern reservoir elevations to temperatures normally prevailing three km deeper. Hot waters in the plume help seal the overlying caprock by depositing silica and clay. More importantly, the plume enhances upward migration of oil from deeper and probably more basinward hydrocarbon source rocks or oil reservoirs.

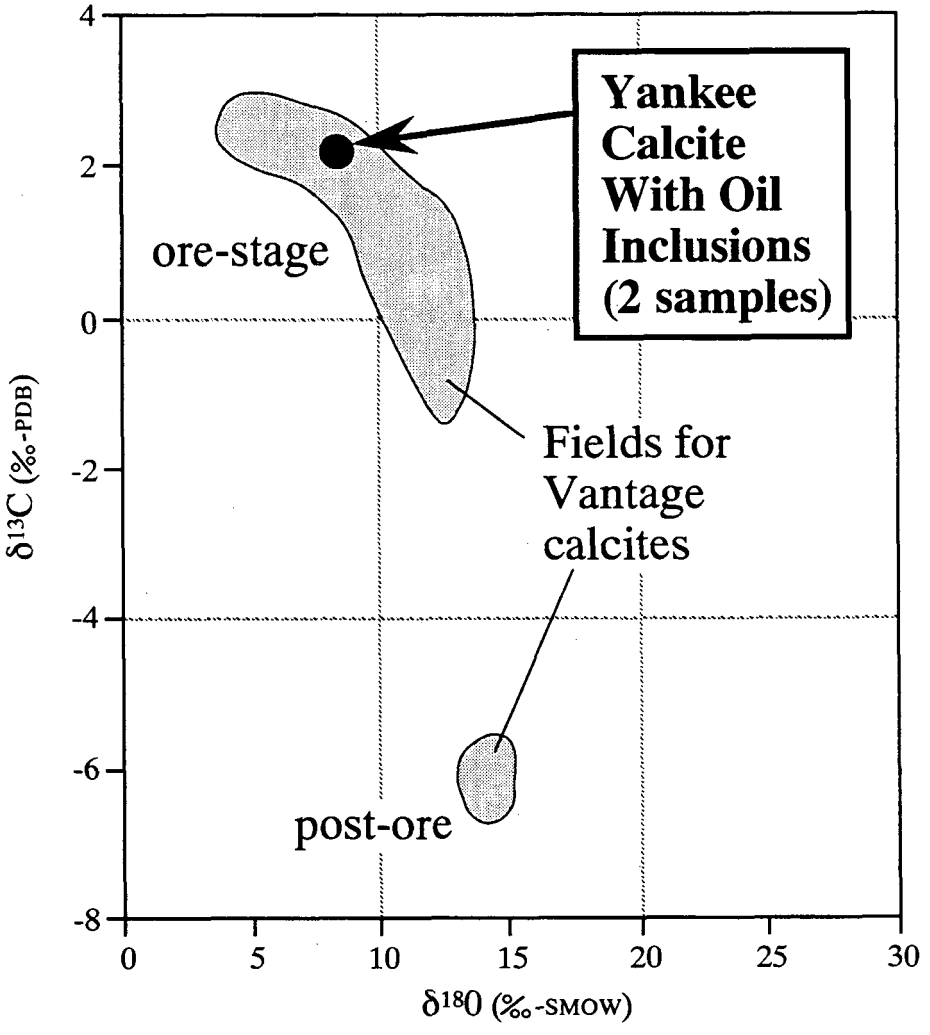


Figure 6. Plot of del^{13}C vs del^{18}O for calcites from the Yankee and Vantage Carlin-type precious metal deposits in the Alligator Ridge mining district, Nevada. The Yankee calcites, which contain large, primary, oil-bearing fluid inclusions, plot within the field for calcites occurring in prominent halos around gold mineralization at Vantage. We conclude from this finding and from field relationships at the Yankee mine free oil occurrence that the oils were probably transported and entrapped in the same hydrothermal system responsible for precious-metal mineralization.

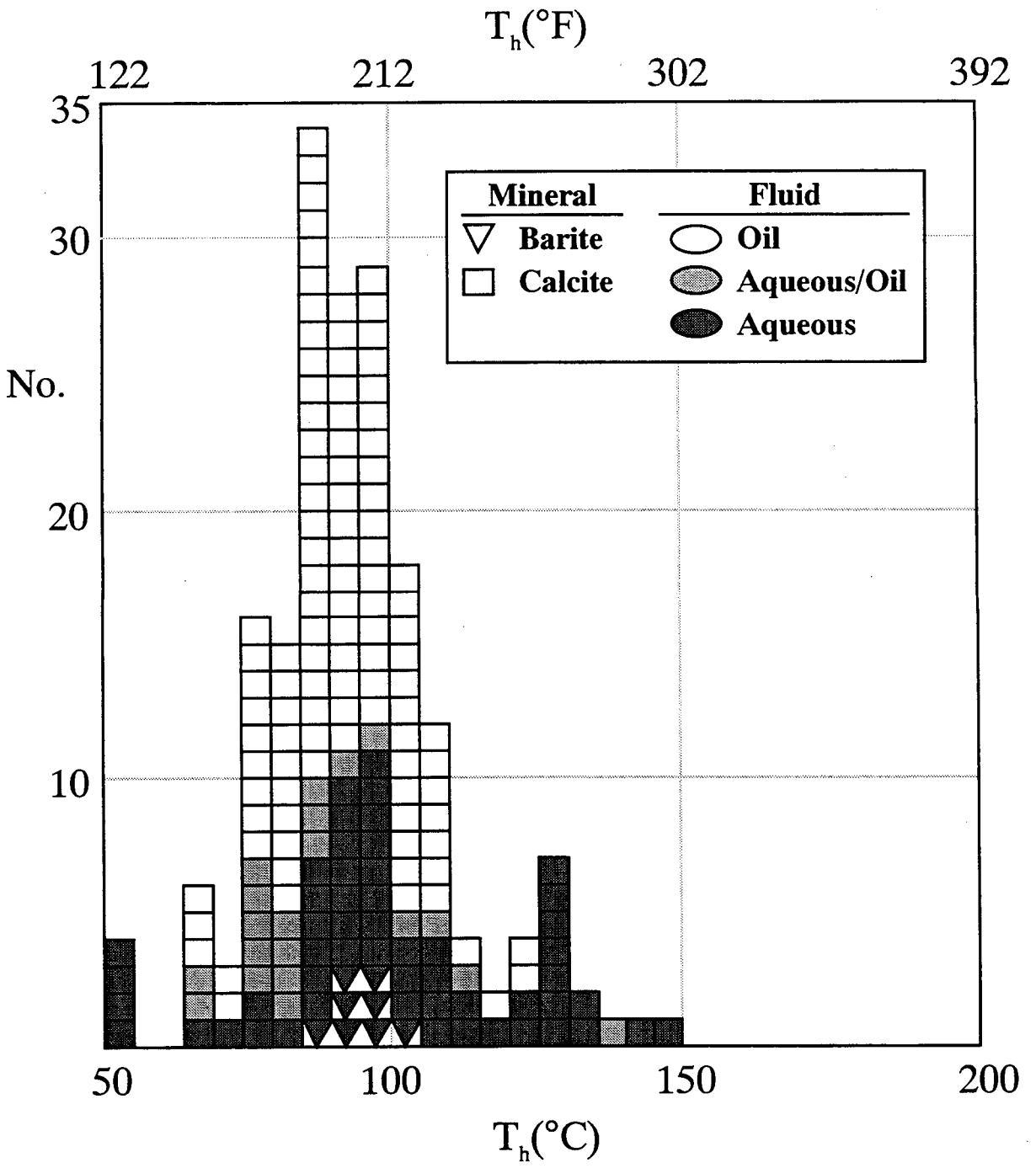


Figure 7. Plot of T_h vs frequency for 188 calcite- and barite-hosted fluid inclusions from the basal Pilot Shale limestone hosting freely-flowing live oil in the Yankee gold mine. The delicate epithermal textures of the host crystals, along with stratigraphic reconstructions, suggest that these T_h are very close to the true fluid-entrapment temperatures. The mean T_h for the oil-bearing, calcite-hosted inclusions, about 95°C, is in the same range as the modern reservoir temperature (121°C) for the oil-transporting geothermal system now circulating at Grant Canyon field.

Mineral Hydrolysis Kinetics

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Dissolution rate laws for silicate mineral weathering can be related to the kinetics of ligand-exchange reactions because the rate-controlling step is cleavage of a similar metal-oxygen bond. The coordination chemistry around the cation is retained in both ligand exchange and in mineral dissolution reactions in most cases. We are testing this relationship with a comprehensive experimental, analytical, and theoretical program designed to measure and characterize the dissolution kinetics of orthosilicate minerals and to incorporate these data in ionic modeling and molecular dynamics (MD) computer simulations of the crystalline solid, the aqueous solution, and the solid-liquid interface. We feel that we have made considerable progress in this project by measuring the dissolution kinetics of orthosilicate minerals with the long-term goal of providing a mechanistic and predictive model of the dissolution process.

To date, we have synthesized, characterized, and measured the dissolution rates for a suite of endmember and mixed-cation orthosilicate minerals (both olivine and willemite structures) as well as a few inosilicate minerals (pyroxenes) over a range of pH (2-8) and temperature (25-70°C) conditions (Casey and Westrich, 1992; Westrich, et al., in press). The dissolution rates of orthosilicates far from equilibrium vary by many orders of magnitude but exhibit a similar dependence on pH and temperature. The dissolution rates appear to correlate well with the rates of solvent exchange around the corresponding hydrated, divalent cation (Figure 1). Simple oxide, orthosilicate, and possibly chain-silicate minerals rank in a similar fashion as the rates of water exchange into the hydration sphere of the dissolved, divalent, metal. Metal-oxygen bond lengths and coordination numbers in all these minerals are similar to those in the hydrated ions. Furthermore, the siloxane (Si-O-Si) bonds are relatively unreactive at low pH's close to the zero point of neutral charge (ZPNC) for quartz, where proton (or hydroxyl) adsorption is limited. Cleavage of bonds between divalent metals and oxygens are thought to exert considerable control over dissolution reactions because proton adsorption onto the silicate surface polarizes these critical bonds, resulting in charge polarization and greater susceptibility to rupture. Rates for

intermediate compounds in a binary orthosilicate series vary approximately exponentially between the dissolution rates for the end-members, which greatly simplifies prediction of the reactivities. Although dissolution rates span several orders of magnitude, our original hypothesis is sustained. Minerals containing alkaline-earth cations dissolve at rates which correlate with ionic size while minerals containing first-row transition metals dissolve at rates which vary with d-electron properties of the cation site and not ion size. Local metal-oxygen bonds clearly exert considerable control over the reaction and this result strengthens a proposed link between the mechanisms of mineral dissolution and the mechanisms by which a dissolved metal exchanges ligands. This correlation, as well as the orthosilicate structure (isolated SiO_4^{4-} tetrahedrons), suggests that silicic acid would be released from the reacting surfaces after protonation and hydration of bonds between divalent metals and structural oxygens. Congruent dissolution of these minerals is confirmed by Rutherford backscattered analysis (RBS) of the near-surface (<5000 Å) of an acid-reacted forsterite crystal (Figure 2), where there is no evidence of silica enrichment nor of cation leaching. In fact, TEM images of acid-reacted phenacite (Be_2SiO_4) show that its crystalline structure extends to the dissolving edge of the crystal. Elastic recoil detection analyses (ERD) of reacted crystals also supports this conclusion. Subsequent to Mn_2SiO_4 dissolution measurements, X-ray photoelectron spectroscopic (XPS) analysis of acid-reacted tephroite powder (Casey, et al., 1993) indicates that surface manganese remains in the divalent state at all experimental run conditions. Other divalent cations (e.g. Fe^{2+} or Co^{2+}) probably behave similarly. In this study, oxidation of multivalent transition metal orthosilicates was suppressed during reaction in order to facilitate comparison of dissolution kinetics over a wide compositional range. Additional RBS, ERD, and Raman analyses of acid-reacted inosilicates ($CaSiO_3$ and $CaMgSi_2O_6$) indicate that there is significant cation leaching, hydrolysis of siloxane bonds, and repolymerization of individual silica tetrahedra in the near-surface region.

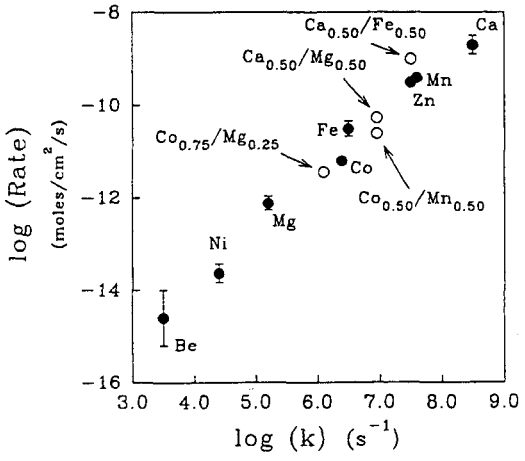

Figure 1. Dissolution rates for orthosilicates at pH=2 and 25°C plotted against water exchange rates about a dissolved cation.

The pH-dependence of the dissolution rate was found to be similar for all orthosilicate minerals at 25°C and presumably relates to variations in the concentration of positive surface charge with pH. The similar variation in Arrhenius activation energies with pH for all

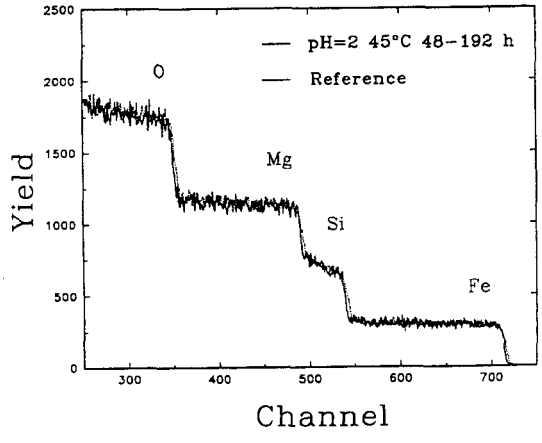

Figure 2. Depth profiles of major elements on reacted and reference surfaces of forsterite.

orthosilicate minerals suggests that the adsorption of protons to surface oxygens contributes a large amount of enthalpy to the activated equilibrium controlling acid-base reactions. The contribution varies with pH as the acid-base properties of the mineral surface vary with temperature. However, the acid-base properties are not particularly sensitive to homovalent substitutions of cations in the mineral structure, even though such substitutions dramatically affect the mineral reactivity and mineral lattice energies.

We have initiated computer modeling of the dissolution process with ionic modeling of the orthosilicate minerals to see if mineral lattice energies correlate with reactivity. The lattice energy, which refers to the total energy of the stable configuration of atoms for a perfect, three-dimensional crystal, can be calculated for very complex minerals (e.g. Burnham, 1985). Lattice energies and configurations of ten orthosilicate compositions of the olivine and willemite structures were determined using observed X-ray-refined cell constants and atomic positions. With the exception of liebenbergite (Ni_2SiO_4), we observe a general trend of increasing lattice energy with decreasing dissolution rate for endmember and mixed-cation orthosilicate minerals at pH 2 (Figure 3). The correlation, however, is not nearly as good as between dissolution rates and solvent-exchange kinetics. The fair correlation between lattice energies and dissolution rates indicates that important interactions are missing from these purely ionic calculations. These interactions include relaxation of bonds among surface atoms, interactions with solvent molecules, and interactions with counterions. Ultimately, we plan to extend and refine these ionic model computer calculations to include minimized structures, shell models, and molecular dynamic (MD) calculations for the orthosilicate series using dissolution data from our experimental measurements. These MD simulations will provide a more realistic atomistic evaluation of the solid-liquid interface and will provide a valuable insight for interpreting the results of the orthosilicate dissolution experiments.

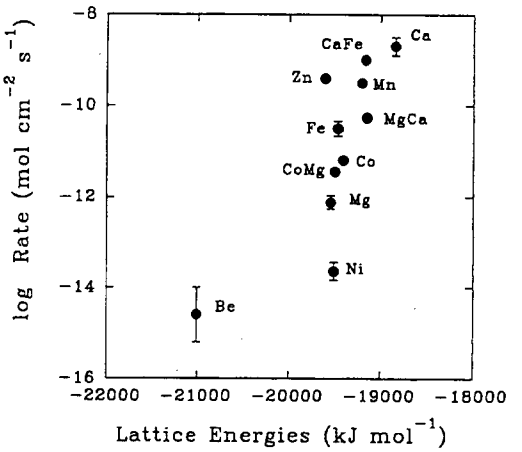

Figure 3. Calculated orthosilicate lattice energies compared to water exchange rates.

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Development and application of new methods for constraining the time of hydrocarbon migration

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The primary objective of the research is to test and assess a paleomagnetic method to date hydrocarbon migration and/or diagenesis of organic matter. This dating method is based on a genetic connection between hydrocarbons/organic matter and precipitation of authigenic magnetite. Isolation of the magnetization carried by the magnetite and comparison of the corresponding pole position to the apparent polar wander path allows the timing of diagenetic events to be determined. The research involves both field and laboratory studies. Several units that contain hydrocarbons (e.g., lacustrine carbonates, Old Red Sandstone, Scotland; Belden Limestone, Colorado) possess secondary magnetizations that reside in authigenic magnetite. Studies are currently underway to determine the relationship between the magnetizations and the hydrocarbons and if the magnetizations date the time of hydrocarbon migration or other diagenetic events. A second objective is to compare another proposed method of dating hydrocarbon migration, Pb-Pb dating, with the paleomagnetic dates we obtain. Organic-rich lacustrine deposits in the Old Red Sandstone which contain a late Carboniferous-Permian chemical magnetization in magnetite also possess a late Paleozoic Pb-Pb age. Laboratory simulation experiments are also being conducted to better understand the mechanism of magnetite precipitation. We are currently focusing on two diagenetic pathways for magnetite precipitation: *in situ* mediated conversion of pyrite to magnetite (which was observed in the Belden) and secondary magnetite precipitation by migrating fluids. The chemical variables that are important for the first pathway have been defined and some experiments performed (e.g., precipitation of ferrous hydroxide gels and conversion to magnetite). The expected results of the research will allow for an evaluation of the paleomagnetic dating method.

Compositional Kinetic Model of Petroleum Formation

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The overall objective of the project is to develop and test models of petroleum generation, migration, and stability. Our first objective is to measure generation kinetics by a variety of experimental techniques, compare the results and geological predictions with each other, and to develop geothermometers that can be used to calibrate paleothermal models used to test the kinetic models. Current efforts concentrate on the kinetics of oil cracking. Our second objective is to develop mathematical techniques and computer programs of varying complexity to predict oil and gas generation, including the effects of maturation on oil composition, and expulsion of the oil from the source rock. The computational approaches are tested against geological data. Reliable modeling can improve oil exploration efficiency, and technology transfer is an important part of this work.

Oil and gas generation kinetics have been measured by a variety of experimental techniques, including isothermal hydrous pyrolysis and temperature-programmed pyrolysis using physical product collection and FID, MS, and TQMS detectors. The non-hydrous pyrolysis kinetics are self-consistent, leading to the conclusion that both individual species and lumped groups (e.g., oil) often require activation energy distribution models to obtain kinetic parameters that extrapolate reasonably to geologic heating rates. Measurements on whole rock samples usually give results that agree well with bitumen-free rocks and isolated kerogens. The resulting kinetics predict generation rates of important products in hydrous pyrolysis, with the exception of CO2. Kinetic analysis of hydrous pyrolysis data is subject to great uncertainties, but kinetics derived from the Rock-Eval potential of hydrous pyrolysis residues agree well with open system kinetics. Even so, the open system kinetics miss some important aspects of geologic maturation. Current pyrolysis experiments are addressing oil stability, initially with hexadecane and then with isotopically labeled hexadecane in several oils. Another area examined was the use of ICP-MS to detect both the source and maturity of oil.

We have incorporated most of our understanding of the oil and gas generation and expulsion processes into a computer program call PMOD. Because different kinetic modeling approaches are appropriate in different circumstances, the program allows the user to interactively construct balanced reaction networks. Several reaction networks of varying complexity have been derived using our and literature data for different kerogen types. The user can choose from four reactor types: an open system, a closed system, a compacting reactor with excess fluid expelled immediately, and a compacting reactor with fluids expelled by a pseudo-1D approximation of Darcy's law. The fourth expulsion model calculates pore pressures and fluid volumes by a modified RKS equation of state. An important consideration in the fourth model is whether the kerogen is considered to be load bearing or pore filling. The model has been tested against geological data in the Maracaibo and Williston Basin. Many of the computational approaches have been adopted by a commercial software vendor, Platte River Associates, and in return for our technical assistance, we have obtained copies of their basin modeling software to use in our research effort.

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1. Project Title

The Role of Mudstones in Burial Diagenesis

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5. Project Overview

A. Specific Project Objectives

1. *Past: :* This project evolved from two decades of research in Gulf Coast Diagenesis. Burial diagenesis of sedimentary basins is driven by the mass and energy transfer that takes place as metastable assemblages of minerals react in the presence of saline water under increasing temperature and pressure. Continental margin basins differ significantly from oceanic basins such as those studied extensively by JOIDES and ODP because very thick deposits can accumulate quite rapidly. Unlike oceanic sediments, sedimentary basins are commonly preserved as part of the continental crust, and thus preserve a record of pre-Mesozoic Earth history. In order to interpret that record, even where it is preserved in high grade metamorphic rocks, it is necessary to understand how sediments are converted into rocks, and what kinds of information are, or are not, rigorously preserved. During burial, fluids transport material (including hydrocarbons) across formational boundaries, and therefore the diagenetic history of any given formation must be studied in relation to surrounding units. For example, "No one believes that the Neogene-reservoired oils are sourced from shales interbedded with the reservoirs. The source of most of the oil and the thermogenic gas in the Neogene reservoirs lies well below current production depths, probably at temperatures above 250-300°F" (SEPM 9th annual Research Conference, 1990). As another example from the Gulf Coast, also true of many other basins, the diagenesis of carbonate rocks is dominated by early meteoric processes. But in almost all cases, the latest cements and replacement phases reflect silicate diagenesis. Thus, carbonate diagenesis cannot be fully understood (or predicted) unless diagenesis in the surrounding silicates is also known, and transport paths between carbonates and silicates must exist.

This long-lasting project originated to document the burial diagenesis of Lower Cretaceous carbonate units in Texas. Recognition of the role of silicate diagenesis in contributing to the late diagenesis of carbonates led to a shift toward documenting the changes which occur in sandstones during burial. The need to understand the mass transfer between sandstones and carbonates, and the need to explain apparent allochthonous diagenetic components in sandstones led to extensive analysis and

compilation of the chemistry of formation waters, and examination of the role of water in accomplishing the observed mass transfer.

2. *Current:* The current thrust is to document the burial diagenesis of Gulf Coast mudrocks, concentrating on three mudrock "types", which display significant compositional differences in the Gulf of Mexico. (1) The (Eocene) Wilcox formation was the first thick clastic unit to be deposited in the Gulf of Mexico sedimentary basin as the result of Laramide tectonism. It consists of relative mature detritus, and it is being studied in central and south Texas, where it reaches temperatures in excess of 200°C. The other two examples of Gulf Coast mudrocks (Oligocene-Miocene) are from the Frio/Vicksburg Formations. (2) In South Texas these rocks were derived from erosion of young volcanic rocks immediately to the west, and thus the sandstones and mudrocks bear a distinctively volcanic signature. (3) In contrast, Frio/Vicksburg-age rocks in Central and East Texas bear a predominantly cratonic signature associated with deposition by the ancestral Mississippi drainage system. Using these three mudstone "types" we are addressing the following questions:

   1. Does a conservative element exist against which gains/losses due to diagenesis can be compared? We are testing Al, Ti, Zr, REE to determine their relative immobilities during burial diagenesis of mudrocks.
   2. What is the cause of the K_2O increase with depth commonly observed in Gulf Coast wells? Can changes in K_2O content be constrained with K/Ar analyses? Is the K_2O increase regional or local in nature? Is the K_2O increase caused by changes in provenance with time, by sorting effects at the time of deposition, or could it be the result of "potassium metasomatism"?
   3. Can other types of analyses (e.g. REE patterns, Sm-Nd model ages, U/Pb isotopic analyses) constrain provenance changes, as well as provide information about other issues such as the accuracy of Sm/Nd model ages in ancient mudrocks, and the source of Pb for MVT-type ore deposits?
   4. Can $\delta^{18}O$ of quartz, coupled with electron-beam-induced luminescence, constrain sources/sinks for SiO_2 in sandstones and mudrocks?
   5. How do the chemical changes documented from cuttings compare to chemical changes in whole core? Do changes in the redox state of iron take place during burial?

3. *Planned:* For the duration of the grant period we intend to concentrate on the following issues:

   1. Identify additional wells in South Texas to constrain the regional distribution of the "potassium anomaly", and conduct analyses on those samples.

2. Continue to characterize the origin of quartz silt using luminescence and oxygen isotopic analysis. This work will expand to the Wilcox Group sediments along the Texas coast and to Miocene sediments along northern Gulf margin. We will continue to assess the role of inherited detrital variability and post-depositional processes in controlling the petrographic and chemical character of quartz in Gulf Coast shales, and to relate conclusions from the study of mudrocks to the problem of quartz cementation of sandstones.
3. Determine chemical variability in well-constrained mudrock samples from conventional cores. A sample set of Miocene shales from the South Pecan Lake Field, Louisiana, has been obtained from Amoco through the assistance of Dr. John Hunt at Woods Hole Oceanographic Institute. A well-constrained data base on porosity, permeability, and pressure trends exists for these samples. Our petrographic and chemical study of these samples will provide information on the mechanism(s) responsible for the trends in physical properties and will improve our understanding of the nature of information preserved in whole rock shales (cores) versus cuttings.
4. A new, and relatively minor, project seeks to establish the physical causes of pressure variation through direct observation of shales within a "seal". Samples for this purpose, from the Ann Mag field in South Texas, have been provided by Dr. Terry Engelder of Pennsylvania State University.
5. Modelling chemical variability in shales. Ongoing work to decipher the roles of primary versus diagenetic variation as the causes of chemical variation in Gulf Coast shales will continue with added emphasis on quantitative mineralogical/chemical modeling, and on utilizing the information contained in trace elemental data.
6. Assessing the role of burial diagenesis in altering the chemistry of mud, so as to compromise interpretation of depositional chemistry based on examination of ancient rocks, both shales and higher grade pelites.

B. Relation of Project to DOE program mission

This project seeks to "...develop a quantitative, predictive understanding of the energy-related aspects of geological, geophysical and geochemical processes within the earth..." (DOE/ER-0249, p. 26), specifically to quantitatively assess the role of mudrocks (shales) in contributing to the mass and energy flux which takes place as sedimentary sequences are buried. Specific topics of interest include the role of mudrocks in providing the material ($CaCO_3$, SiO_2, acid, etc.) which affects reservoir porosity in sandstones, the scale (from diffusion-path-limited to extra-basinal) over which mass transport takes place, and the degree to which burial diagenesis modifies depositional signatures (e.g. K_2O content, Sm/Nd and U/Pb).

C. Relation to other DOE-funded projects

We are coordinating some of our analyses with Dr. John Hunt (WHOI), who is interested in petrographic data which bear on the problem of "pressure compartmentalization", and with Dr. B. Mack Kennedy (LBL) who is conducting noble gas analyses on a suite of samples for which formation water analyses are available.

6. Scientific and Technical Content

Despite the fact that mudrocks constitute approximately 2/3 of all sedimentary rocks, mudrocks have not received proportional research effort. The efforts of the late John Hower and his group in the mid 1970's stand as a milestone, and subsequent efforts have primarily been directed at clay mineralogy, especially as revealed by transmission electron microscopy. No group, within or outside of industry, has conducted, or is conducting, a sustained investigation of a major sedimentary basin such as the Gulf of Mexico, or systematic chemical and petrographic analyses of suites of mudrocks from the Gulf of Mexico sedimentary basin. Pronounced elemental mobility in shales is documented by an increasing number of studies and is the focus of work being done by several groups in both academia and industry as summarized in a February Geotimes article by Dave Pevear and in a recent paper by Awwiller (JSP 63: 501-512). The DOE-funded portion of our work ties in with a more comprehensive research program on basinal diagenesis that includes work on Cenozoic shales of the Iberia Abyssal Plain (Milliken, ODP), on volume changes associated with low grade metamorphism of the Stanley shale of the Ouachita Mountains (Land and S. Sutton, NSF), and on foreland basin sandstones and shales in the southern Appalachians (Milliken, ACS) and in the northern Apennines (McBride and Milliken, NSF).

Until we understand mass and energy transport in sedimentary basins, our ability to predict practical factors such as reservoir porosity, and hydrocarbon generation and trapping mechanisms will remain empirical. Mudrocks constitute most of the fill of sedimentary basins, and until their role is quantified, we cannot hope to build useful predictive models of sedimentary basin evolution.

This research is still in the "data-gathering" stage. The questions being addressed (5.2.1 through 5) will, ultimately, enable the "scale if system closure" to be determined for specific components. As examples: (1) Is the K_2O increase observed in many (but not all) Gulf Coast wells the result of transfer of K_2O from sandstones, or are additional factors involved? Clearly the isochemical K_2O system extends beyond the confines of the mudrocks, and includes both mudrocks and sandstones. But on what scale? (2) Many Gulf Coast mudrocks lose $CaCO_3$ with increasing depth. Gulf Coast sandstones contain allochthonous $CaCO_3$ cement, which, in many cases, has $^{87}Sr/^{86}Sr$ values similar to

coeval marine carbonate such as that deposited in coeval mudrocks. But the volume of $CaCO_3$ lost from mudrocks seems to considerably exceed the volume of $CaCO_3$ emplaced in sandstones, and so the "scale of system closure" seems to exceed the local sand-shale system. (3) Do mudrocks gain or lose SiO_2, and do all three examples of mudrocks under study behave similarly? (4) What is the fate of components like Li and Pb which are clearly lost from the mudrocks (relative to Al, Ti, Zr, and REE) during burial diagenesis - what is their scale of transport, and what sinks can be demonstrated?

State of the art petrographic and isotopic techniques are being directed at the problems under investigation by this project. In some cases these techniques have never been applied to mudrock diagenesis, or to questions of material transport between mudrocks and sandstones. These techniques include:

A: Electron-beam-induced luminescence combined with back-scattered electon and standard petrographic imaging. Electron-beam-induced luminescence is accomplished on a JEOL T330A scanning electron microscope equipped with an Oxford Instruments detector, as well as on a JEOL 722 electron probe equipped with an in-house luminescence detector system. In addition to Gulf Coast mudrocks, we are systematically re-examining Gulf Coast sandstones in the area of study and will be pursuing additional studies of the $\delta^{18}O$ of quartz overgrowth cements based on our observations.

B: Thermal ionization mass-spectrometry is being used to determine REE patterns, and to assess whether or not the "Eu anomaly" which appears as the result of extensive feldspar dissolution can be used as a diagenetic tracer. Sm/Nd systematics are being used as provenance indicators, and are REE being tested as "immobile" elements. The reliability of Nd model ages in mudrocks is being tested not only to assess provenance variations in the rocks under study, but to determine the extent to which burial diagenesis alters Nd model ages. U/Pb systematics are being used to constrain provenance, as well as to assess Pb mobility and possible sinks for Pb released by feldspar dissolution.

C: Laser heating of silicate samples as small as 1 mg in a BrF_5 atmosphere is being used for $\delta^{18}O$ analyses. Quartz and kaolinite are now analyzed routinely, but chlorite currently yields unreliable results. Additionally, samples smaller than about 1 mg yield erratic results. A new vacuum line is under construction, and these problems will be further researched.

7. Project Output

Milliken, K. L., 1992, Petrographic documentation of reactions affecting detrital feldspars in mudrocks: American Association Petroleum Geologists Annual Meeting, p. 89.

Wood, J. R. and **Milliken, K. L.,** 1993, Plagioclase diagenesis in subsiding basins: Geological Society of Canada/Mineralogical Society of Canada, Joint Annual Meeting, Abstracts, in press.

Compound-specific carbon isotopic analysis of petroleums

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Issues being addressed and their significance:

The general issues being addressed are those involved with determining and interpreting the chemical and isotopic changes associated with petroleum maturation. Current attention is focussed on compound-specific isotopic data. Specific issues include baseline studies to establish the range of isotopic variation in individual compounds in crude oils, and the origins of specific compounds in oils. These are significant issues because of their fundamental importance to the process of petroleum generation. Also, the techniques developed for compound-specific isotopic analysis of petroleums are also directly applicable to problems involving organic contaminant transport in the environment.

Importance of solving the problem:

The solutions of the problems being addressed are of importance from a basic science perspective as well as from a DOE mission perspective. This program is contributing to a better understanding of petroleum maturation. Such knowledge has direct applications in energy-related technologies including petroleum exploration and exploitation.

Project Output

Calibration and standardization of the gas chromatography isotope ratio mass spectrometry system (Bakel and Ostrom, in press). This was accomplished by analyzing a series of n-alkanes with known $\delta^{13}C$ values under a broad range of chromatographic conditions. Special attention was paid to the effect of a natural background signal (unresolved complex mixture) on the isotopic measurements of individual compounds. These studies are significant because they demonstrate that good chromatographic separation is the limiting factor for generating high quality compound-specific isotopic data, and that high quality data can be obtained for compounds in the presence of a natural background signal.

Other measurements were made to test for any isotopic fractionation during preparatory silica gel liquid chromatography. Overall, it was determined that the presence of petroleum background or preparatory chromatography had little or no effect on the $\delta^{13}C$ values for n-alkanes. It was further concluded that the accuracy and precision of these measurements were ±0.5‰ or better. This work was necessary before any other measurements could be made.

Isotopic characterization of branched and cyclic hydrocarbon biological marker compounds in petroleums from the Uinta Basin, Utah (Ruble et al., in press). This work was accomplished by analyzing individual compounds from the petroleums which had been chemically characterized by collaborators at the University of Oklahoma (Tim E. Ruble and R. Paul Philp). These data are significant because they demonstrate that biological markers thought to be derived from bacterial matter (e.g. hopanes) were enriched in ^{12}C relative to compounds thought to be derived from algal material (e.g. steranes). Details of the ecology of the depositional environment of the Green River Shale (the source rock for the petroleums studied) are inferred from such data.

Oil-oil and oil-source rock correlations in the Illinois basin using compound specific isotopic analysis (Bakel and Risatti, in prep and Bakel et al., in press). The initial phase of this study was accomplished by determining the $\delta^{13}C$ values of the n-alkanes present in several oils which had previously been correlated to three different source rocks in the Illinois Basin. It was discovered that, based on the $\delta^{13}C$ values of their n-alkanes, the oils examined could be split into three families. The isotopically determined families corresponded perfectly with families determined previously using biological marker data, and could be related directly to their source rocks. Crude oils from the Phillipstown (IL) field were analyzed in the same manner. The $\delta^{13}C$ values of the n-alkanes show that the Phillipstown oils correlate with some of the oils in the initial study and are probably generated from the New Albany Shale. Further study of the oils suggests that differences in the molecular composition of these oils are due to low levels of microbial degradation.

Isotopic composition of hydrocarbons (C_4 to C_{19}) in oils from western Canada. These measurements were accomplished using a specific chromatographic scheme designed to resolve the complex mixture of low molecular weight hydrocarbons in crude oils. This is a significant study because it allows us to obtain isotopic data on a variety of compounds (n-alkanes, aromatic, branched and cyclic hydrocarbons) in the C_4 to C_{19} range. In addition, previous studies on these oils show that they span a range of maturities and were generated from very similar source material, making this an excellent set of samples for a natural maturation study. The data will be interpreted in terms of changes as a result of maturation and in terms of the origin of these low molecular weight compounds. Several trends have been observed in this set of data: (1) the $\delta^{13}C$ values of n-alkanes and isoprenoids become higher with increasing maturity, (2) for several molecular families (n-alkanes, isoprenoids and cyclohexanes) low molecular weight members are isotopically lighter than their high molecular weight counterparts, and (3) cyclopentanes are isotopically heavier (by 3-5 per mil) than any other compounds in the crude oil. Using the comprehensive molecular and geological data available on these oils through collaborators at Exxon Production Research Co., these observations are presently being interpreted in terms of petroleum generation processes.

Bibliography of publications emanating from this project:

Bakel, A. J., Dyer, R. M., Ruble, T. E. and Philp, R. P. (1993) Carbon isotopic composition of n-alkanes and isoprenoids in slightly biodegraded crude oils from the Phillipstown Field (Illinois Basin). Accepted for publication as extended abstract in the proceedings of the 16th International Meeting on Organic Geochemistry.

Ruble, T. E., Bakel, A. J. and Philp, R. P. (1993) Compound specific isotopic analysis of Uinta Basin native bitumens. Compound Specific Isotope Analysis in Biogeochemistry and Petroleum Research. (in press)

Bakel, A. J. and Ostrom, P. H. (1993) Evaluation of accuracy of carbon isotopic measurements for individual n-alkanes by gas chromatography/isotope ratio mass spectrometry. Compound Specific Isotope Analysis in Biogeochemistry and Petroleum Research. (in press)

Bakel, A. J. and Risatti, J. B. (1992) Oil-oil correlation in the Illinois Basin by compound specific isotopic analysis (CSIA). Abstract #159, American Chemical Society National Meeting. San Francisco, CA, April 5-10, 1992.

STABILITY OF NATURAL GAS IN THE DEEP SUBSURFACE

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The main objective of the research has been to establish deep gas composition, and to understand the factors controlling the distribution of methane and other gases in the subsurface at depths down to 50,000 ft or more. Initial attempts to establish deep gas composition involved thermodynamic calculations. It became clear, however, that it was important to compare the predicted gas composition with that actually present. Fluid inclusions appeared to offer one way of obtaining deep gas samples, but their analysis is complicated by their small size and the common occurrence of multiple populations formed at different times. I felt that the only way to avoid this difficulty was to analyse each individual fluid inclusion separately. The original analytical system used a single quadrupole mass spectrometer and an Apple computer. Subsequently the experience gained with that system was used to design and build a dual mass spectrometer system with high speed ADC and improved computer capabilities (Alliant, HP/Apollo).

We are now using a combined theoretical and experimental approach to develop an understanding of deep gas composition and the factors that control it. Fluid inclusions provide small samples of gas that were trapped in crystals which grew in the deep environment, such as overgrowths and fracture-filling cements. We have developed a method for analyzing the gases in individual fluid inclusions using a fast-scanning, computer-controlled, dual mass spectrometer system. The bursts of gas released when individual fluid inclusions rupture on heating in vacuum are analyzed in 25 msec (Figure 1) and the data stored on magnetic tape. Subsequent offline processing provides the composition of each inclusion (background corrected)(Figure 1 top), as well as monitoring total gas release as a function of temperature (Figure 1 bottom). In addition populations of inclusions can be presented on appropriate ternary diagrams. From 10 to 1000 individual fluid inclusions have been analyzed in a variety of 10 mg samples.

The dual mass spectrometer system is currently being upgraded with a 16-bit ADC. This will provide a 16-fold increase in dynamic range. An improved calibration line that provides pure gas samples and known gas mixtures is in the final stages of construction. Although minor modifications continue, efforts to develop analytical techniques are essentially complete, and we are about to make the transition from analytical chemistry to geology. While many samples have already been analyzed the main emphasis has usually been on system development and evaluation. In future the techniques will be applied to geologic problems. While most technical issues related to the analysis of individual inclusions have been solved, at present it is not possible to provide a gas analysis for a specific individual inclusion (e.g. one recognized and described microscopically). We are evaluating the possibility of building a system to rupture individual inclusions.

Deep gas composition is also being calculated thermodynamically using a free energy minimization program that can handle up to 70 components in 20 phases. We have completed a detailed study of clastic reservoirs including those

with feldspars, clays, iron oxides, carbonate cements, and anhydrite. Reservoirs initially containing oil that was later cracked to methane will also contain a graphitic residue, and we have modeled reservoirs both with and without graphite. In general the presence of graphite enhances methane stability. With increasing depth of burial large quantities of carbon dioxide are formed by the thermal breakdown of carbonate cements and this can dilute other components and reduce them to trace levels.

These theoretical and analytical methods are being applied to samples from the Arkoma basin, the Powder River basin, and other areas including the deep Gulf Coast. We have also analyzed a wide range of samples from many different geographic areas in cooperation with other research groups. The combined capabilities are well illustrated by a study of the Arkoma Basin of Oklahoma and Arkansas. The past deep burial and thermal history of the basin was established using the commercial *BasinMod* program and adjusting burial history and thermal regime to optimize agreement between calculated and observed vitrinite reflectance. Arbuckle carbonates in deep cores from the Arkoma basin were thin sectioned and fluid inclusion filling temperatures measured optically. Some inclusions show a graphitic residue consistent with the basin's deeper burial in the past. Inferred past temperatures and rock mineralogy were used to calculate equilibrium gas compositions thermodynamically, and in many cases these resemble the gas composition determined mass spectrometrically for different inclusion populations in fracture-filling cements.

The deep gas research program impacts the DOE's ability to accurately establish the Nations natural gas reserves. As natural gas becomes a more important fossil fuel (because of its availability and its low environmental impact) a realistic estimate of future reserves is critically important. The research will help in deciding whether the deep unexplored parts of basins have economic potential. For example, the deepest 20,000 ft of the Anadarko Basin, Oklahoma, are essentially undrilled, and from an exploration perspective this is a frontier basin. In better explored basins the research will help in predicting areas of non-economic (or less economic) gas that has high carbon dioxide or hydrogen sulfide content.

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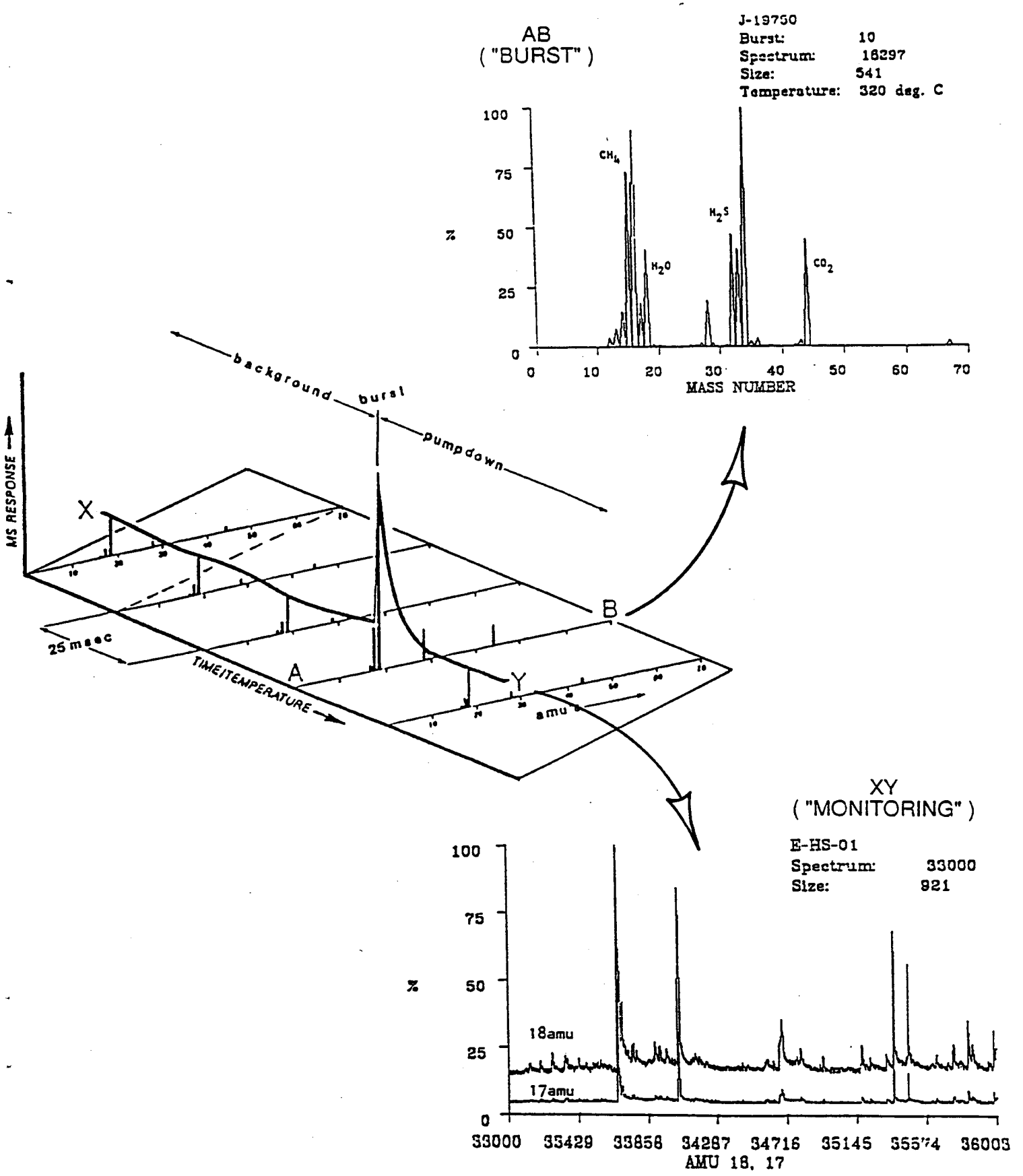

Figure 1

(Center) Schematic diagram showing the scanning of sequential mass spectra through time; (Top) Mass spectrum corresponding to an individual fluid inclusion burst; (Bottom) Release of water as a function of time showing bursting inclusions over approximately one minute.

PROJECT:

GEOCHEMICAL INCORPORATION OF SULFUR INTO SEDIMENTARY ORGANIC MATTER

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1. Objectives: Sulfur is believed to be involved in preserving organic matter in sediments, in converting this organic matter to petroleum and in controlling the timing of petroleum generation from a source rock. The fundamental geochemical issue in this matter is the mechanism of sulfur incorporation into sedimentary organic matter. Although there is compelling evidence to indicate that reactions of reduced inorganic sulfur species with organic molecules occur during the early stages of diagenesis and under very mild conditions, the molecular mechanisms are still not well understood. There are several important geochemical questions in this issue: what forms of sulfur and organic matter react to form the organically-bound sulfur in sediments; what and how sedimentary variables influence the kinetics of sulfur incorporation; and why and how the abundance and forms of sulfur differ in various geologic environments. Previously, hydrogen sulfide has been considered to be the primary sulfur reactant for organic sulfur formation in sediments. Recently, evidence is emerging that H_2S oxidation products, especially polysulfides, are also important. The roles of elemental sulfur, sulfite and thiosulfate in the formation of organic sulfur are still not clear. The broad research objectives are (1) to elucidate the mechanisms of natural sulfurization process at a molecular level regarding both sulfur and carbon reactants, (2) to study the changes in the abundance and forms of sulfur during early diagenesis in various organic-rich sedimentary environments, and (3) to examine the influence of sulfur incorporation in the preservation of sedimentary organic matter. In this context, the following geochemical problems are currently being tackled: detailed studies of sulfur speciation in different types of organic-rich marine sediments (for example, coastal and salt marsh locations); mechanistic studies on organic sulfur formation; and mechanistic studies on sulfide oxidation. An important goal of this project is to use synchrotron-radiation-based x-ray absorption near-edge-structure (XANES) spectroscopy for characterization and determination of sulfur species, in addition to other state-of-the-art techniques. XANES spectroscopy has a unique advantage over other techniques, including chromatography, because it is matrix insensitive and provides both qualitative and quantitative information of all the different forms of sulfur present in a sample. Currently, an important part of our research is focused on developing or improving analytical techniques based on XANES spectroscopy and chromatography for the determination of important sulfur species, including polysulfides and sulfonic acids.

2. Scientific issues currently being addressed and their significance: This project, which is aimed at understanding the formation and transformation of sedimentary organic sulfur during early diagenesis, has four major components: (1) studies of sulfur speciation in sediments, (2) mechanistic studies of organic sulfur formation, (3) mechanistic studies of sulfide oxidation to understand the formation of different oxidation intermediates, and (4) analytical methods

development. Since these are interdependent areas of the research, we have taken the approach to tackle them in parallel to achieve the best possible output. Specific issues currently being addressed under the different sub-topics are elaborated in some detail below.

(I) Sulfur speciation in field samples: Sulfur speciation is currently being studied in detail in sediment core samples from three different organic-rich locations with high rates of H_2S formation from bacterial sulfate reduction: (1) intertidal sediments from Great South Bay, Long Island, New York; (2) salt marsh sediments from Flax Pond, Stony Brook, New York; (3) off the coast of Peru. The Peru sediment samples were obtained on a cruise from October-November 1992 from three sites at 11°, 12°, and 13° south within transects that ranged from 100 m to 1000 m water depths; these samples will be provided by T. Eglinton (WHOI) who will collaborate in this effort. This study is important for assessing (1) how the abundance and forms of sulfur differ in various depositional environments, (2) the relative role of hydrogen sulfide and its oxidation products in the incorporation of sulfur into organic matter, and (3) the effect of sulfur incorporation in the diagenesis of organic matter.

Our recent studies suggest that in near-surface sediments a significant fraction of organic thiols is bound to the particulate phase through polysulfide linkages and can be released as original thiols by treating with a disulfide cleaving reagent. The nature of particles which serve as attachment points for polysulfides in sediments is not known; however, we speculated that organic structures rather than inorganic particles (silica ?) are probably involved. It is possible that humic structures coated on mineral surfaces probably serve as substrates for attaching thiols through polysulfide linkages. Studies are being carried out to understand whether humic substances are involved in incorporating polysulfides and in attaching thiols in sediments. We use x-ray absorption fine-structure spectroscopy and FT-IR spectroscopy for characterizing the chemical structures in these studies.

(II) Mechanistic studies of organic sulfur formation: We will carry out a systematic study to examine the molecular parameters of organic molecules which affect reactivity with sulfur nucleophiles. A series of functionalized organic compounds, in which the number and positions of unsaturation vary systematically will be studied to better understand the sulfur addition mechanism. Effects of conjugation and substitution at the α and ß positions of the double bond with various electron donating/withdrawing groups (e.g alkyl and phenyl groups) will be examined. The reactivity of the organic compounds with sulfur nucleophiles will be investigated by studying the nature of the products formed as well as the reaction kinetics. Sulfur nucleophiles to be examined will include H_2S, polysulfides, sulfite and thiosulfate. Characterization of organic sulfur compounds formed in these experiments will be carried out by both x-ray sulfur edge spectroscopy and chromatographic techniques. XANES results will provide important bulk level characterization of the products as thiols, thiolanes and thiophenes. Based on this data set, we may perform detailed structural analysis of the organosulfur compounds, on selected samples, using chromatographic techniques.

Sulfonic acids in sediments. The mechanisms of sulfonic acid formation in sediments is not well understood, although there are several potential pathways: (1) oxidation of thiols or organic sulfides, (2) addition of sulfite to activated carbon-carbon double bonds and (3) transformation of thiosulfonic acid. Laboratory kinetic studies will be carried out using model compounds to examine the relative importance of the different pathways.

(III) Mechanistic studies of sulfide oxidation: Recently, using XANES spectroscopy, we have obtained preliminary evidence for the formation of a +2 oxidation state intermediate

in the Ni^{2+} catalyzed oxidation of aqueous sulfide. This is an exciting finding because a +2 oxidation state inorganic sulfur species has never been detected previously, although the formation of such a species has been predicted theoretically. Currently, studies are in progress to characterize this +2 oxidation state intermediate using FT-IR spectroscopy and XANES spectroscopy. Paul Marshall from the university of Northern Texas is performing theoretical *ab initio* calculations of the infrared frequencies to aid in the identification of the structure of this species by matching with the experimental infrared peak data. Future studies will examine the effects of other transition elements, such as Co(II), Cu(II), Zn(II) in forming this intermediate. We will study the role of this intermediate in the subsequent formation of other oxidation products, especially polysulfides.

(IV) Developing/improving analytical methods:

An HPLC method for polysulfides. So far, we have used XANES spectroscopy for the determination of polysulfides. Although this method has several advantages (for example, lack of H_2S interference), it does not offer adequate sensitivity for the determination of aqueous-phase polysulfides in sediment pore waters. The attempts to develop an HPLC technique for polysulfides, using precolumn derivatization with fluorescent reagents, including N-(7-dimethylamino-4-methyl-3-coumarinyl) maleimide, have been unsuccessful due to interference by a number of reagent related peaks and probably those due to reactions with sulfide. Thus, we will examine post-column derivatization combined with ion-pair separation of polysulfides. Since aqueous-phase polysulfides are expected to be dianionic species, we will use dionium reagents, including pentamethylenebis(trimethylammonium), pentamethylenebis(triphenyl-phosphonium) as ion-pairing agents. Fluorescent reagents (for example, 4-(6-methylnaphthalen-2-yl)-4-oxobuten-2-oic acid) or UV-visible reagents (for example, 2,2'-dithiobis(5-nitropyridine)) will be examined for post-column labelling.

3. Experimental and theoretical approach: The distribution and speciation of polysulfides and other important sulfur species, including hydrogen sulfide, organic sulfides, thiols, thiophenic sulfur, and iron sulfides (especially pyrite) will be determined in a variety of organic-rich sediments. The x-ray absorption fine structure spectroscopy will be used for gross-level characterization of the various sulfur forms (for example, pyrite, polysulfides, thiophenic sulfur etc.) in sediment core samples. The x-ray absorption spectra are to be taken in beam line X-19A at the NSLS. The XANES technique will be complemented with chromatographic and colorimetric techniques for sensitive and selective determination of various types of sulfur compounds. For example, the Cline's colorimetric method will be used for the determination of hydrogen sulfide in sediment pore water samples. We will develop a HPLC method for sensitive determination of polysulfides distributed in both aqueous and particle-phase of sediments. The HPLC method based on o-phthalaldehyde fluorescence derivatization will be used for the determination of thiols. In addition to XANES spectroscopy and chromatographic techniques, we will use FT-IR spectroscopy for determining sulfur speciation. FT-IR spectroscopy using the CIRCLE CELL (Spectra-Tech, Stamford, Connecticut) based on the cylindrical internal reflection technique will be used for analyzing aqueous samples. Sediment-core samples from Great South Bay, Long Island, will be obtained from anoxic, near-shore regions using polybutyrate or stainless-steel core tubes. Cores will secured, sealed, and returned as quickly as possible to the laboratory for processing. The same technique will be used for sampling sediments from salt-marsh locations. Sediment samples from the Peru upwelling region will be provided by Dr. T. Eglinton (WHOI), who will collaborate with us in these

studies. The sediment cores will be extruded and sectioned in an anaerobic glove box; pore water will be separated from the sediment by either anoxic centrifugation.

4. Importance of solving the problem being addressed by this research: Currently, there is widespread interest in sulfur cycles from a biological, geochemical, biogeochemical, and environmental viewpoint. In the area of sulfur geochemistry in marine sediments, most past studies have emphasized inorganic aspects such as pyrite formation, and there is a paucity of information regarding interaction of sulfur with organic matter. Thus, this project aimed at obtaining a more complete understanding of the formation and transformation of organic sulfur in marine sediments during early diagenesis is timely. This research is of academic as well as industrial interest. An improved understanding of polysulfides incorporation into organic matter will provide important insights regarding the mechanism of petroleum generation from source rocks because the occurrence of polysulfide linkages in kerogen can markedly affect the kinetics of maturation reactions. A better understanding and the ability for predicting the chemical form, abundance and distribution of organic sulfur in fossil fuels can lead to improved practical applications in a number of areas such as: (1) guiding fossil fuel exploration, especially for oil and gas with a concern for fuel quality; (2) understanding why different oils behave differently during processing; and (3) developing improved processes and uses for fossil fuels.

The information generated in this research may provide important insights into organic matter diagenesis and the effect of sulfur incorporation on the preservation of organic matter in sediments. New and improved techniques for sulfur species determination will result from this study. For the first time, our research has provided experimental evidence for the formation of a +2 oxidation state intermediate (sulfoxylate ion). This new sulfur species warrants further research from the viewpoints of both basic and applied chemistry. The new knowledge on the chemistry of polysulfides in sub-oxic sediments and the methods developed for polysulfides will prove to be very valuable in many areas of geochemistry and environmental chemistry, including corrosion, anoxic transformation of organic pollutants and sub-surface chemistry of transition metals.

5. Major recent accomplishments: This project began in FY 1992. Major advances made so far are listed below and are expanded in sections that follow.

1. Studies on the occurrence of particle-bound polysulfides in sediments.
2. Determination of polysulfides by XANES spectroscopy and studies on their formation from the oxidation of aqueous H_2S under conditions of high sulfide-to-oxygen ratios.
3. Mechanistic studies on sulfide oxidation and the detection of a novel +2 oxidation state intermediate.
4. A study describing new oxidation states of +1 and -5 for the two different sulfur atoms in thiosulfate.
5. Studies on sulfur speciation in sediments and the first-time detection of sulfonic acids as important organic sulfur constituents.
6. Improvement in the procedures for x-ray absorption spectroscopic analysis for the determination of sedimentary sulfur species.

Details of Element 1. This study carried out in collaboration with K. Mopper (Washington State University) and B. F. Taylor (University of Miami) describes for the first time that a

significant fraction of inorganic polysulfides is bound to the particulate phase in sediments and can react with carbon-carbon unsaturated bonds in organic matter, thereby attaching it to the particulate phase through polysulfide linkages. In this study we used the α,β-unsaturated compound acrylic acid as a probe to examine the distribution and reactivity of inorganic polysulfides in sediments. The attachment to the particulate phase through polysulfide linkages may affect the bioavailability of the reactive organic matter in sediments and hence may play an important role in the preservation of organic matter in anoxic marine sediments. The ongoing studies of sedimentary sulfur species from an organic-rich coastal site (Great South Bay in Long Island, New York) and from a salt marsh (Flax Pond in Stony Brook, New York) indicate that in fact the dominant fraction of hydrophilic thiols (e.g., 3-mercaptopropionic acid) is present in binding with sediments.

Details of Element 2. In previous studies, sulfide oxidation has been conducted mostly as pseudo-first-order reactions with limiting sulfide concentrations and the formation of polysulfides was not observed under those conditions. Thus, we examined the formation of polysulfides from sulfide oxidation with excess sulfide and limiting oxygen concentrations, conditions typically present in organic-rich reducing sediments. We used XANES spectroscopy for the determination of aqueous-phase polysulfides. Time-series experiments were conducted using a 0.1 M NaHS solution in deionized water and in 0.7 M sodium chloride solution at room temperature (25 ± 1°C). The initial pH was adjusted to be in the 8.0 - 8.5 range. The effects of sea sand, Fe^{2+}, and Ni^{2+} on the rate of oxidation were examined. We observed significant formation of polysulfides only in the series with added Ni^{2+}. These results suggest that catalysis by transition elements such as Ni^{2+} is probably important for the formation of polysulfides in marine sediments.

Details of Element 3. In sulfide solutions containing added Ni^{2+}, a striking feature has been the presence of a peak at 2476.1 eV in the spectra of the initial oxidation period. After about 100 hours of air oxidation, this peak completely disappeared in both deionized water and 0.7 M NaCl solution media. Based on the linear correlation between sulfur oxidation state and peak energy reported in previous studies, the position of this peak corresponds to an oxidation of +2. However, there is no inorganic sulfur compound with a +2 oxidation state of sulfur, although in organic sulfoxides sulfur is present with a relative charge density of +2. Previous studies postulate that oxidation proceeds probably through the formation of an intermediate HSO_2^- having a +2 oxidation state sulfur, but so far there has been no experimental evidence for its formation. Studies are being continued (experimental approach using FT-IR spectroscopy and theoretical *ab initio* calculations) to characterize this novel sulfur species.

Details of Element 4. We used XANES spectroscopy to clarify an anomaly in the widely-held view regarding oxidation states of sulfur atoms in thiosulfate. In anoxic sediments, thiosulfate undergoes a novel type of energy metabolism known as disproportionation which has been described as an inorganic fermentation pathway involving an intramolecular redox change. However, it is difficult to envisage a redox mechanism in thiosulfate disproportionation because, according to the currently held view, the two sulfur atoms in thiosulfate exist in the oxidation state of sulfate (+6) and sulfide (-2) and do not change their respective oxidation states upon disproportionation. We have shown using XANES spectroscopy that the oxidation states of the sulfur atoms in thiosulfate are in fact +5 and -1, which support a redox mechanism in the disproportionation of thiosulfate to sulfate and sulfide.

Details of Element 5. XANES analysis has revealed that sulfonic acids constitute a significant fraction of the organic sulfur compounds in near-surface sediments from Great South

Bay, Long Island. Organic-rich sediments from the Peru Margin also showed the same. These results are very significant because sulfonic acids have not been found as major constituents in any previous study, probably due to analytical limitations. Laboratory studies are being pursued to understand the origin of this class of compounds in sediments.

Details of Element 6. Quantitative analysis of sulfur species from XANES data is based on the method developed by Dr. Penner-Hahn from the University of Michigan. This method involves fitting of a normalized sample spectrum with linear combinations of spectra of appropriate model compounds, using a non-linear least-square procedure. For this purpose, we have gathered XANES spectra of pure standards of various types of sulfur compounds, including those containing polysulfide linkages. We examined the accuracy of the method for quantitative analysis using mixtures of several standard compounds. The results suggest that the analytical error is less than 5% if correct standards have been chosen for fitting. We have continued to improve the techniques for preparing samples for XANES analysis. For example, the silica matrix poses a unique problem in the analysis of sediment samples, and we have addressed this issue by using a 75/25 weight percent mixture of quartz and $CaCO_3$ as matrix for standards. The analysis of sediment extracts as solutions of the organic extractant (such as CH_2Cl_2) packaged in x-ray film bags often caused problems, including bursting of the bags from solvent evaporation when exposed to x-rays. These problems are now alleviated by evaporating the organic extract on a glass fiber filter under a stream of nitrogen and using it in a dry form for analysis.

6. Bibliography of publications emanating from this project:

* Vairavamurthy, A., Zhou, W. and Manowitz, B. Observation of a +2 oxidation state sulfoxylate ion intermediate in the Ni(II) catalyzed oxidation of aqueous sulfide. Submitted to *Nature*.
* Vairavamurthy, A., Manowitz, B., Zhou, W. and Jeon, Y. Determination of hydrogen-sulfide oxidation products by sulfur K-edge XANES spectroscopy. In The Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Volume, in press (1993).
* Vairavamurthy, A., Zhou, W., Manowitz, B. and Eglinton, T. Organic sulfur compounds in marine sediments: information from XANES spectroscopy (abstract). Extended Abstract for a presentation at the *16th International Meeting on Organic Geochemistry*, Stavanger, Norway, Sept. 1993.
* Vairavamurthy, A., Manowitz, B., Luther, III, G. W. and Jeon, Y. Oxidation state of sulfur in thiosulfate and implications for anaerobic energy metabolism. Geochimica et Cosmochimica Acta 57, 1619-1623, 1993.
* Eglinton, T.I., Irvine, J., Sinninghe Damste, J.S., Schouten, S., de Leeuw, J.W., Vairavamurthy, A. and Manowitz, B. Formation and diagenesis of macromolecular organic sulfur in Peru margin sediments (abstract). Submitted for a presentation at the *16th International Meeting on Organic Geochemistry*, Stavanger, Norway, Sept. 1993.
* Vairavamurthy, A., Manowitz, B. and Jeon, Y. A study of sulfide oxidation at sub-molar concentrations in aqueous solution using XANES spectroscopy. Presented at the symposium on the *Environmental Geochemistry of Sulfide Oxidation*, American Chemical Society Meeting, Washington, DC, Aug. 1992.
* Vairavamurthy, A., Mopper, K. and Taylor, B. F. Occurrence of particle-bound polysulfides and significance of their reaction with organic matters in marine sediments. Geophysical Research Lett. 19, 2043-46 (1992).

1. **Project Title** Organic Geochemistry/Continental Margin and Deep Ocean Sediments

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Scientific and Technical Content

Relation of this research to research being conducted by others in the field.

Application of knowledge gained from organic geochemical research increases the probability of finding oil substantially. However, with recent downsizing of many industrial exploration groups, developing and applying these techniques advantageously is left, by default, to academic and government laboratories. Our group has focused on development and application of organic geochemistry to a variety of geological problems, with particular emphasis on gases - amounts, compositions, time-temperature regime of formation, and influence on fluid migration processes in sedimentary basins.

Results from laboratory hydrous pyrolysis experiments are being compared to field data to determine the amounts, relative distributions, and kinetics of gas generation (i.e. C_1-C_6 hydrocarbons, CO_2, H_2S, H_2) during maturation of organic-lean rocks from the Louisiana Gulf Coast of North America. Presently, there exists little reliable data of this type, which is critically important to estimating depths and amounts of natural gas potentially available in sedimentary basins. Furthermore, generated gases may play an integral role in expulsion and migration of petroleum and may also create and destroy rock permeability as a result of numerous chemical and physical processes. In addition, gases generated at depth could be a significant contributor to sediment overpressuring, causing episodic opening of faults as permeability channels to oil and gas migration.

Over the years of the project, we have collaborated with a wide variety of other industrial, government and academic laboratories in obtaining and sharing data, samples, and analytical techniques. These collaborations have been and continue to be valuable in providing ideas, samples, and expertise from industry, government, and academic scientists on needed research which the oil industry is unable to undertake or complete because of budget and personnel limitations.

Most recently, we helped to form and have became the lead organic geochemical arm of a consortium of university and industrial laboratories, the Global Basin Research Network (GBRN). The scientists in the initial group were all interested in gaining a better understanding of dynamic sedimentary basin processes, particularly those related to subsurface fluid flow. These processes can be best understood if sedimentary basins were viewed as chemical reactors. However, the problem is difficult because basins are typically hundreds of kilometers in size. In addition, their operation links many different processes, each of which has become a separate scientific discipline. A better understanding of fluid movement in basins requires 1) the development of basin process models that integrate the effects of sedimentation, structural deformation, temperature, fluid flow, inorganic, and organic chemical change, and 2) the assembly of a unified multi-disciplinary data base on process-representative portions of specific basins that is accurate enough to test these models. Progress requires the linking of scientists from diverse disciplines in collaboration with explorationists from oil companies willing to provide the necessary data. The GBRN was founded in January 1990 to meet these challenges. It currently includes scientists from nine academic institutions (including Cornell University, The Lamont-Doherty Earth Observatory of Columbia University, The Louisiana state University, Michigan Technological University, The Woods Hole Oceanographic institution, and Texas A & M), several companies specializing in various aspects of computer modeling and visualization (including Sun Microsystems, IBM, and Computational Mechanics), and 11 oil companies. The

ultimate goal of the research is to develop a general methodology of process visualization/modeling which can be applied to understanding fluid flow processes (including gas and oil accumulation) in any sedimentary basin.

Our collaboration with the GBRN has shown us that the wide variety of hydrocarbon parameters currently used in oil exploration are also very useful in constraining more general fluid flow processes around and beneath sedimentary basins. For example, our collaboration with Dr Larry Cathles at Cornell, an expert in inorganic geochemistry and modeling, suggests that methane dissolution of gas may be an important mechanism of oil migration below about 10,000 ft at pressures greater than 200 bars (Whelan, Eglinton, and Cathles, in press; funding from the Gas Research Institute), even in relatively organic lean rocks such as those typical of the Tertiary Gulf Coast. Also, as part of the GBRN research funded under this grant, we have integrated the large petroleum correlation study assembled by the Texas A & M GERG group for a 20x40 km area of the off-shore Louisiana Gulf Coast into the comprehensive geological/geophysical visual data base (or "data cube") provided by the GBRN. The hydrocarbon data strongly support the hypothesis initially put forward based on cumulative geological and geophysical data: that oil and gas injection into stacked reservoirs is occurring episodicly at the present time into the highly productive EI-330 reservoirs. As a result, funding has been obtained by the GBRN from the Fossil Energies Division of DOE to engage in "test" drilling (in collaboration with several oil companies) into the EI-330 "feeder" tubes as a test of this "dynamic injection hypothesis". The goal of this new project, due to start about June, 1993, is to critically evaluate powerful new visualization techniques developed by the GBRN along with drilling of such "dynamic" systems as a potentially valuable new oil and gas exploration strategy.

The goals of fossil energies-DOE research are very specific and focus only on samples and fluids to be obtained during new drilling in EI-330 scheduled to begin this summer. The broader aspects of the GBRN organic geochemical research are being funded by DOE-BES under this project. This broader research, as described here, includes: a) examination of maturity of rocks and compositions of oils and gases from the surrounding areas, such as nearby block SMI-128 which does not seem to be undergoing dynamic injection; b) development of new methods required to better define migration pathways and effects of temperature anomalies on Gulf Coast sediment kerogens; and c) hydrous pyrolysis experiments.

Schedule of major research activities.

i) Hydrous pyrolysis experiments are being carried out to determine amounts, relative distributions, and kinetics of gas generation (i.e. C_1-C_6 hydrocarbons, CO_2, H_2S, and H_2) during maturation of representative rocks from the Louisiana Gulf Coast of North America and the Alaskan North Slope.

ii) Hydrous pyrolysis rock buffer experiments are being carried out to determine if water (rather than just kerogen) is contributing hydrogen to oil and gas formation.

iii) Insertion of hydrous pyrolysis data on rates and thermodynamics of gas generation into GBRN sedimentary basin process model under development on supercomputer at Cornell. The data from the Woods Hole hydrous pyrolysis experiments, along with existing literature and other data on kinetics of oil and gas generation and migration (such as that of Braun and Burnham from the Lawrence Livermore Laboratory and data such as that reviewed in Hunt and Hennet in the attached reprint) are in the process of being incorporated into a simple 1-D maturation model developed by Dr Larry Cathles at Cornell (Whelan, Eglinton, and Cathles, in press). In the future, this and other data will also be incorporated into the three dimensional process models currently under development by Cathles and coworkers as part of the GBRN on the supercomputer at Cornell.

iv) Visualization of organic geochemical data for a 20x40 km area of the South Marsh Island/Eugene Island area of the Louisiana Gulf Coast in its correct 3-dimensional geological and geophysical setting. The Woods Hole group is responsible for integrating new and existing organic geochemical data into this "data cube" of the GBRN. We have already transferred a considerable amount of existing petroleum hydrocarbon data (obtained

primarily from the Texas A & M GERG group) into geological workstations (Landmark Graphics) at Lamont. This organic geochemical data can now be overlain on any of the geological, geophysical, geochemical, temperature, or pressure data which also resides in the workstation. Most of this Woods Hole GBRN work has been funded from our current DoE Basic Energy Sciences grant.

The most startling result to date from this research to date has been that oil and gas injection appear to be occurring into Gulf Coast reservoirs at Eugene Island Block 330 (EI-330) at the present time. Current research is focusing on determining the best organic geochemical indicators for "seeing" and quantitating these "dynamic" fluid injection events, including examination of how reservoir hydrocarbon compositions at EI-330 are changing over time. For comparison, we are also examining similar data for the nearby SMI-128 block, where there is no evidence for similar dynamic injection. In addition, compound specific isotopic analyses of gases and oils in both EI-330 and SMI-128 are currently being measured by Dr Martin Schoell of Chevron so that we will be able to better define the relation of these oils to each other

v) New techniques. The research utilizes source and maturational information from kerogen, gas, and oil to learn more about the nature of these "dynamic injection processes" in comparison to "normal" oil and gas migration processes in the surrounding areas. New organic geochemical methods are being developed and calibrated to aid in this research, using funding only from DOE-BES These include:

a) Compound specific isotope GCMS studies of EI-330 oils to see if they represent one or several source facies (in collaboration with Dr Martin Schoell of Chevron)

b) High resolution pyrolysis-MS (py-MS) and pyrolysis-GCMS (py-GCMS) matching of oil asphaltenes and potential source rock kerogens from EI-330 and SMI-128. Because of numerous chemical similarities, asphaltenes are currently thought to be small chunks of kerogen Therefore, an oil-oil and oil-source correlation technique using these two components could potentially provide a valuable new correlation tool not subject to many of the current problems of biomarker correlations, such as effects of preferential expulsion of specific compounds and biodegradation effects. In addition, the technique might be useful in eliciting migration pathways, because the polar asphaltenes tend to be "dropped out" of oils along the migration pathway between the source and the reservoir

c) TG-FTIR - tracing migration pathways and rock maturity via NH_3 Oil migration has been found to give anomalously high concentrations of ammonia in clays along the migration pathways in BES sponsored research of Williams. We have determined that TG-FTIR recovers most of the sediment nitrogen (Whelan, Seewald, and Eglinton, in press). We have received samples from Williams which will be used to see if TG-FTIR can be used to trace oil migration pathways and give an indication of the time-temperature history of the nitrogen in the associated rocks along the migration pathway, as suggested by previous results from our laboratory. In addition, when applied to source rocks, TG-FTIR simultaneously provides the maturity as well as the gas and oil generation potential of the kerogen in the rock via the pyrolysis peaks for methane and higher hydrocarbons (Whelan, et al, 1988 and1990).

d) (future) New organic petrographic techniques, including examination of kerogens in whole rocks of the Gulf Coast and Laser-microscopy-pyrolysis-GC and -GCMS.

<u>Scientific or technical issues currently being addressed and their significance.</u>

<u>i) Hydrous pyrolysis experiments:</u>

a) Amounts and compositions gases available for geologic processes. This data is critical to determination of depths and amounts of gases potentially available in sedimentary basins both as a resource and as potential agents for geological change and fluid migration processes. Very little data of this type is currently available.

b) Rock buffer experiments - determination of whether water (rather than just kerogen) is contributing hydrogen to oil and gas formation. This is an important issue because

hydrogen availability limits the depth to which gas can form. If the necessary hydrogen could be derived from water, rather than just kerogen as generally believed at the present time, then gas could potentially be formed at greater depths than previously believed.

c) Quantitatively, how much gas is potentially available in basins containing various kerogens types? Is amount sufficient for high pressure solubilization of oil in methane at high pressure as proposed initially by Price? Our recent research suggests that even fairly organic lean sediments (with as little as 0.4% TOC) may be capable of generating sufficient gas to trigger these processes (Whelan, Eglinton, and Cathles, in press). These hydrous pyrolysis experiments on Gulf Coast rocks will help to constrain these numbers better in future research.

d) Incorporation of hydrous pyrolysis data, along with existing literature data, in 3-D computer process models currently under development at Cornell as part of the GBRN, will help to show how organic and inorganic geochemistry interact with geology and geophysics in basin processes. Results are being compared to actual data visualized as part of the GBRN "data cube" (described below).

ii) GBRN - visualization of organic geochemical data superimposed on a 3D geological and geophysical framework provided by the GBRN "data cube" as described above. Organic geochemical indicators of dynamic fluid flow processes currently under investigation for EI-330 oils include: anomalously high gas and oil production, anomalously high amounts of highly biodegradable light hydrocarbon gas coexisting with biodegraded oils, anomalous C7 hydrocarbon compositions, and temporal changes oil and gas compositions in reservoirs over periods of a few years. All of these features are consistent with recent condensate injection into EI-330 reservoirs (Whelan, Kennicutt, Brooks and Schumacher, paper to be presented at European Association of Organic Geochemists meeting, Stavanger, Norway, Sept, 1993). Our discussions with oil company scientists lead us to believe that these features are frequently located along the shelf edge of the Gulf Coast as well as in many other basins worldwide, suggesting that such "dynamic injection events" may be very widespread.

Importance of solving the problem being addressed by the research.

Our collaborations of the past several years, particularly as part of the GBRN, has shown us the importance of using a variety of organic geochemical parameters to understand more general fluid flow processes around and beneath sedimentary basins. Such understanding is crucial because sedimentary basins are the low-temperature chemical reactors that produce most of the hydrocarbons, minerals, and drinking water resources upon which modern civilization depends. For the next several decades there is probably no science or technology more important to the nation than that related to the discovery and production of these subsurface fluids. These fluid flow processes undoubtedly also play an important role in basic geological processes in sedimentary basins (e.g., overpressuring, fracture opening, and the creation and destruction of porosity).

Gas generation plays a critical role in sedimentary basin processes being studied by the GBRN. However, rates of gas formation and expulsion from sediments, gas migration paths, maturation window, kerogen characteristics required for gas generation are not nearly as well known as those for oil. Our laboratory and field research focuses on defining compositions, amounts and rates of formation of gases present in marine sediments and petroleum basins. Presently, there exists little reliable data of this type, which is critically important to estimating depths and amounts of natural gas potentially available in sedimentary basins. Furthermore, generated gases may play an integral role in expulsion and migration of petroleum. For example, gaseous solution of oil may be an important mechanism for oil transport, particularly in areas containing generally low organic carbon rocks, such as the U.S Gulf Coast (Whelan, Eglinton and Cathles, in press). Generated gases may also create and destroy rock permeability as a result of numerous chemical and physical processes. In addition, gases generated at depth could be a significant contributor to sediment overpressuring, causing episodic opening of

faults as permeability channels to oil and gas migration, as currently being studied by the GBRN for the EI-330 reservoirs in the Louisiana Gulf Coast. In order to evaluate the quantitative importance of these processes, a critical need is knowing the amounts, compositions, and rates of formation of gases from kerogens and oils. In addition, hydrous pyrolysis mineral buffer experiments are addressing the question of the depth to which gas can be generated.

In the last 15 to 20 years, application of knowledge gained from organic geochemical research has substantially increased the probability of finding oil in comparison to drilling a structure without ancillary geochemical data. At the present time, as it becomes more critical to find and exploit new reserves of domestic oil and gas, many oil companies are downsizing and cutting their exploration groups at an alarming rate. Thus, oil companies no longer have the resources to explore new organic geochemical techniques useful in exploration or even to explore extending applications of existing methods. Laboratories such as ours, particularly working in collaboration with the larger consortium such as the GBRN, can fill this critical need.

Project Output

Major recent accomplishments with supporting data and their significance.

i) Hydrocarbon distributions in EI-330 reservoirs, particularly the presence of condensates together with biodegraded oils, anomolous C7 hydrocarbon patterns, and changing hydrocarbon distributions over time, are consistent with very recent injection of condensate into these reservoirs, possibly at present time. In discussions with oil company scientists, similar hydrocarbon patterns are very widespread all along the shelf edge of Gulf Coast. This "dynamic hydrocarbon injection hypothesis", or active injection of hydrocarbons into reservoirs at the present time as proposed by the GBRN provides a coherent explaination for these hydrocarbon distributions, as well as for many other puzzling aspects of the geophysical and geochemical data in the region.

ii) Through hydrous pyrolysis and on-line sampling techniques, we have determined that enough methane is generated even from organic-lean Gulf Coast sediments to be able to form a separate gas phase and solubilize oil at P>200 bars (Whelan, Eglinton, and Cathles et al., in press). These experiments have also shown that carbonate free Gulf Coast rocks and Woodford Shale samples generate substantial amounts CO2 and methane thoughout hydrous pyrolysis experiments. The amounts are high enough so that this source of gas must be considered in various basin processes (e.g. overpressuring, fault opening an closing, creation and destruction of permeability, etc.).

iii) Hydrous pyrolysis experiments using rock buffers strongly suggest that hydrogen needed for gas generation in sedimentary basins could be coming from water, rather than just from kerogen. If water is a significant source of hydrogen in gas formation, then much gas could be generated in much deeper horizons than previously thought possible.

iv) Development of TG-FTIR of methane as an excellent way of measuring gas generation potential and maturity of sedimentary rocks, including those which are very organic lean or at very high maturities (Whelan et al, 1990). Measurement of ammonia using the same technique appears to provide a matuation indicator for rocks which contain little or no organic carbon, information important in basin studies (Whelan et al., 1988 and unpublished results).

v) An excellent set of downhole temperature measurements, vitrinite reflectance values, kerogen NMR maturity values, and TG-FTIR analyses of ammonia have been obtained for sediment rocks and kerogens isolated from the Middle Valley hydrothermal area at the northern end of the Juan de Fuca Ridge in the eastern Pacific (Whelan, Seewald, and Eglinton, in press). This sample and data set provide an excellent calibration for thermal maturity data for other organic lean continental shelf and slope sediments, including those from the Gulf Coast.

vi) Measurement of reflectance on indigenous vitrinite in polished thin section has shown that this may be the preferred method of measurement for Gulf Coast sediments. The procedure allows much better distinction between indigenous versus recycled vitrinite than was previously possible with kerogen isolates (L.B. Eglinton, unpublished results).

vii) John Hunt has published two papers utilizing a graphical procedure for estimating the depths of the oil and gas windows, which can be used by geologists with no computer. Required input data are estimates of burial history along with kerogen type and sulfur content for the sedimentary rocks under consideration.

viii) Electron paramagnetic resonance (EPR) power saturation measurements appear to give a very clear indication of beginning of oil window (Dickneider, Whelan, and Blough, submitted). If trends observed for the test wells prove to be general, these measurements would provide the oil industry with a very simple and operator independent measure of the beginning of the oil window.

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Dickneider, T.A., J.K. Whelan, and N.V. Blough (submitted) EPR study of kerogens from three Alaskan North Slope wells. To be submitted to Organic Geochemistry

Direct Speciation of Metal and Metalloid Ions by Optical Spectroscopies

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We are using an integrated suite of spectroscopies to directly investigate the geochemistry of metal and metalloid (Al/Si) complexation and its subsequent effect on petroleum reservoirs, hydrologic transport, ore deposits, and water-rock interactions. The latter interactions are responsible for rock weathering and system permeability, which in turn have implications in economic geology (e.g. oil recovery efficiency) and environmental geology (e.g. waste repository integrity). During the course of our investigations of inorganic and organic complexants, the organic species themselves have become an interesting and tractable issue. By studying organics in fluid inclusions, the diagenetic history of an oil field, including oil maturation and migration, can be interpreted. This information may be useful in the further search for and production of oil.

Specific systems we have examined to moderate temperatures (up to 150°C) include palladium(II)-chloride and -organic acid complexation; silicon, aluminum, and ferric competition for oxalate; arsenic sulfide complexation; and REE (actinide waste surrogates) -organic acid complexation. Organic acids / conjugate bases studied for complexation include simple carboxylics such as acetate, oxalate, and citrate and which are known to be present in significant amounts in natural settings such as sedimentary basins. We are presently starting a preliminary survey of organics in oil-filled fluid inclusion samples from Pine and Railroad Valleys (NV) and the Guaymas Basin to evaluate new techniques such as microscope-based luminescence and Raman spectroscopies.

Our technical approach centers around the use of optical spectroscopies such as Raman vibrational, Uv/Vis electronic absorption (conventional and ultra-sensitive photoacoustic methods), and luminescence spectroscopies to directly examine the complexation mechanism, even in complex matrices and and with competing processes. Note that due to the low solubility of some of the species (e.g. REE-organics), the sensitivity afforded from photoacoustic methods is required to get relevant data. Furthermore, we are extending these techniques to probe individual fluid inclusions with micro Raman and micro luminescence techniques to directly compare laboratory results with natural reservoir systems. NMR

has also been utilized where necessary; however, more extensive integration with the optical spectroscopies has been limited by present funding levels.

Palladium(II) chloride speciation studies were initiated to understand trace metal migration / deposition mechanisms. This work involved systematic changes in pH, chloride concentration, and temperature. Using the Pd-Cl background information, ligand competition studies between chloride and organic bases for palladium have shown strong organic-base complexation, confirming speculation for a role for organics in trace metal transport in low temperature systems. Figure 1 shows the ligand replacement of chloride by showing the decreasing strength of the ligand (Cl^-) to metal charge transfer band in the absorption spectrum as well as the Pd-Cl stretch in the Raman vibrational spectrum. This result compliments the bulk solubility studies performed by Scott Wood (University of Idaho). All together, PGE's are proving to be more mobile than previously expected, and this laboratory conclusion is being corroborated by new field studies.

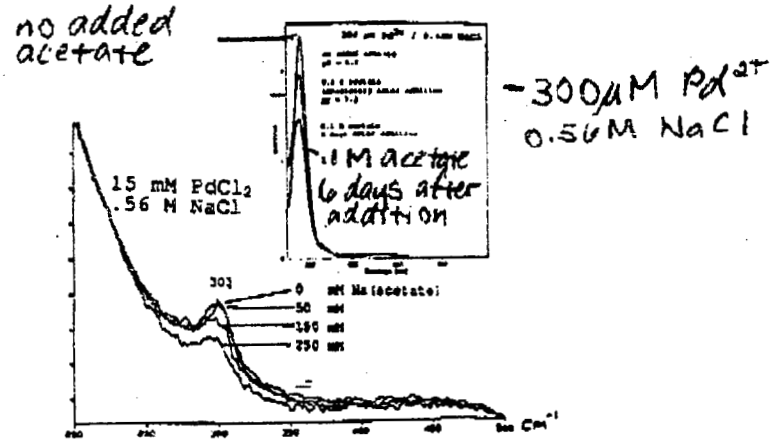
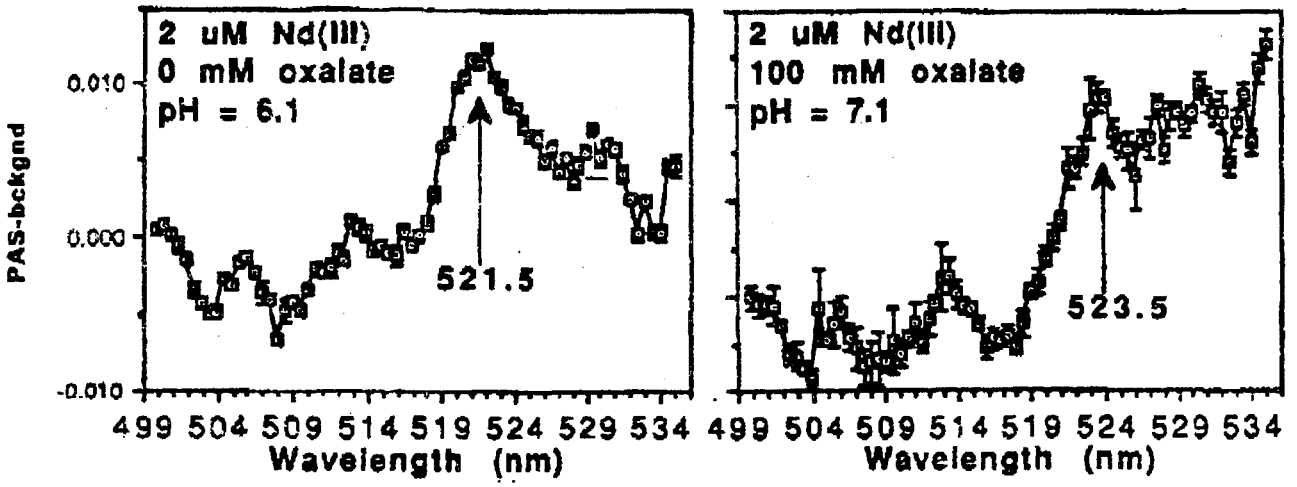
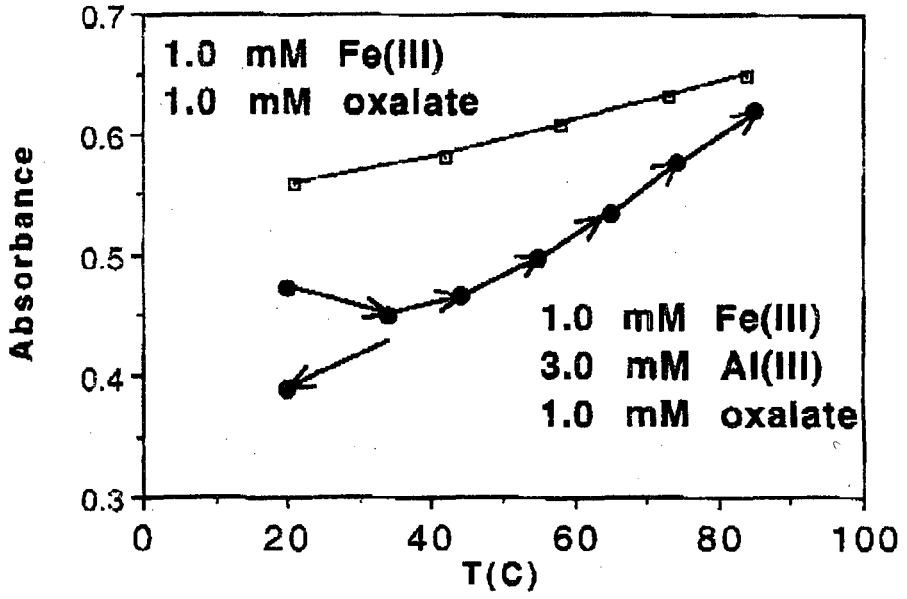


Fig. 1

Raman and absorption spectra were found for As-S and REE-acetate species this past summer during Scott Wood's sabatical. While much data analysis remains to be done, the Raman spectral signatures obtained (peaks at 333, 385 [high sulfide], 400, 420 [low sulfide] cm^{-1}) give us insight into the species present under different conditions. The primary candidates implicated from solubility studies (Eary, 1992) include AsS_x^{3-2x} ($2 \le x \le 4$) and, especially, the dimeric species $H_2As_3S_6^-$. While this system may have some environmental justification, it is primarily of basic geological significance due to the co-occurrence of As and precious metal (i.e. gold) deposits. REE behavior, on the other hand, may enable better modelling of the closely related actinides found in spent fuel rods and other nuclear wastes. The search for a range of safe disposal methods for such waste is an important DOE environmental issue. To see whether we could study these actinide surrogates at anything approaching environmental concentrations, we obtained the photoacoustic spectrum of Nd-oxalate complexes, with solubility < 5 μM and absorption < 0.00002, and shown in Fig. 2. Unlike many other systems, little temperature dependence was noted to 75°C for any of these complexes (either As-S or REE-organics).



Careful infrared and ^{13}C NMR studies have disproven previously claimed silicon oxalate complexation as a "silicon ester" (Marley et al., 1989), even to 175°C (see our recent submission to Org. Geochem. included in publication package). Therefore, a different mechanism must be found to account for field evidence (Bennett and Siegel, 1987) for silicon dissolution in neutral pH, high organic oil waters. Because of the ubiquitous nature of silicon rock matrices, silicon dissolution has implications for permeabilities of fossil fuel reservoirs and waste containment sites and therefore needs to be understood. By way of contrast, aluminum was found to form strong complexes with oxalate, even more so at higher temperatures and consistent with molecular modeling. In order to quantify these temperature dependent results, we ran a competition experiment between Fe^{3+} and Al^{3+} for oxalate. As shown in Figure 3, the absorption of the $Fe(ox)^{+}$ complex shows that iron out-competes aluminum for oxalate at higher temperatures, approaching a point near 100°C where the presence of Al^{3+} is barely noticeable. (The initial drop with temperature may be due to lack of equilibration at room temperature.) This experiment shows that even though Al-ox complexes become stronger at higher temperatures, caution must be employed before drastic aluminosilicate dissolution is invoked in organic rich diagenetic systems where competitive elements may also be present.



Finally, we have embarked on the analytical development of microscopic attachments for Raman and luminescent measurements of organics in fluid inclusions. A Raman microprobe is a commercial addition that has recently (8/92) been successfully installed for use in the visible wavelength region. However, because of the luminescence problem associated with excitation of organic-rich FIs with visible light, we have been altering the basic instrument for use in the extreme red / near IR spectral region. This wavelength region should minimize photoluminescence (and photodecomposition). To compliment the Raman vibrational data, advantage of the organic photoluminescence can be obtained by using a microscope to collect luminescent data. However, while luminescence spectroscopy is very sensitive, it typically produces broad spectra which do not distinguish individual species in mixtures found in naturally occurring FIs and even in bulk samples. Although not specifically diagnostic, even these broad spectra can be informative, and the determination of the tristimulus values (based on the International Commission on Illumination (CIE) chromaticity diagram) from the luminescence has been correlated with the maturity of the oil trapped in FIs (the luminescence from more mature oil is bluer than from less mature oil) (McLIMANS, 1991).

A technique to deconvolve broad luminescence spectra into individual or class-specific contributions involves synchronously scanned luminescence (LLOYD, 1971). In synchronously scanned luminescence, both the excitation and detection monochromators are scanned together through the spectrum, with the detection monochromator a constant wavelength lower than the excitation monochromator. The resulting cross correlation between excitation and luminescence spectra causes sharper peaks, with widths of tens of nanometers (full width half height), sharp enough to be used as a fingerprint for organics or classes of organics. For macroscopic bulk samples, this method has been demonstrated in the classification and identification of aromatic containing products such as gasoline, kerosene, oil, asphalt, and coal components (WAKEHAM; 1977; JOHN and SOUTAR, 1976; DICK and KALKREUTH, 1985), and we are presently adapting the technique to direct interrogation with a microscope.

Testing the correlation between sequence stratigraphy, seismic reflectors and diagenetic changes in carbonates: Implications for the distribution of porosity and permeability

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Sedimentary successions from two core borings (Unda and Clino) through the Neogene to Recent margin of western Great Bahama Bank display a repetitive pattern that is interpreted to be the record of sea level changes. The development of geometries of corresponding seismic sequences is also interpreted to be the result of fluctuations in sea level. This interpretation is in agreement with the lithologic indications of sea level changes. There is also a strong correlation between the diagenesis and the seismic sequences. Seismic sequence boundaries coincide paragenetic sequence boundaries and with changes in mineralogy. The correlation of surface-bounded changes in diagenesis to the seismic data strongly indicates that sequence geometries control the pathways of diagenetic fluids.

In general, the seismic sequences coincide with facies successions but many of the facies changes within the slope section would be too subtle to create the necessary impedance contrast for seismic reflectors. Subsequent diagenesis enhances the contrast between different sedimentologic packages. Hardground development is probably the most significant change as it creates a hard, dense layer that is then overlain by loose sediment providing an abrupt velocity change and thus the necessary impedance contrast for a seismic reflector. Further velocity variations are created during later diagenesis by selective cementation, dissolution and compaction, which enhances or decreases small original sedimentologic velocity changes leading to the required velocity contrasts for a seismic reflection pattern.

The carbonates of Unda and Clino show no direct correlation between acoustic properties (p- and s-wave velocity) and age or burial depth of the sediment. Sonic velocity is rather controlled by the combined effect of depositional lithology and several post-depositional processes, such as cementation or dissolution, that create carbonate specific rock-fabrics. As a result velocity inversions are common along diagenetic horizons. These impedance contrasts are responsible for the seismic reflector at these boundaries.

In the investigated carbonates, Vp ranges from 1700 to 6600m/s and Vs ranges from 600 to 3500m/s. This range is mainly caused by variations in the amount of porosity and the pore type. Carbonate mineralogy has no direct correlation with velocity. Completely dolomitized rocks are among the fastest but also the slowest samples of the dataset. Velocity is the result of the type rather than the amount of dolomite: fabric destructive micro-sucrosic dolomitization decreases velocity dramatically whereas fabric preserving, crystalline mimetic dolomitization results in very high velocities. In general, the measured velocities show a positive correlation with density and an inverse correlation with porosity, but departures from the general trends of correlation can be as high as 1500 m/s. This large scattering in the velocity is an effect of carbonate specific pore-types. The elastic properties of the different pore-types explains why rocks with the

same porosity can have completely different velocities. For example rocks with a dominant moldic porosity have velocities which are over 2500 m/s faster than same porous rocks with mainly interparticle porosity. The different pore-types form during specific diagenetic stages, and, thus, the velocity of individual horizons is directly related to diagenesis.

In both cores paragenetic sequences coincide with seismic sequences. The paragenesis of each of these zones is largely a factor of (1) the original sediment composition, (2) the water depth at the time of deposition and (3) the subsequent sea level fluctuations. The interplay between these factors govern the development of permeability and the types of fluids (meteoric or marine) to which they are exposed. These diagenetic horizons control pathways of fluid circulation concentrating diagenesis along sequence boundaries. For example, the development of hardgrounds during periods of low sedimentation results in the formation of well cemented impermeable horizons which later can act as aquatards controlling fluid flow. Variations in mineralogy related to early diagenesis are also evident across seismic boundaries. Typically increases in dolomite are present below sequence boundaries. Across two boundaries, the dolomite content increases sharply from an usual background value of 5-10% to maximum values of over 50%, then decreases downhole to more typical background values. All paragenetic sequence boundaries and the surfaces across which mineralogical changes occur do coincide with seismic sequence boundaries (Fig. 1). This correlation of surface-bounded changes in diagenesis indicates that changes in sea level alter the diagenetic potential of the carbonates within the sequence stratigraphic pattern. Because the diagenetic processes control the development of porosity and pore types and thus the permeability, fluid flow pathways are largely controlled by stratal geometries and might be predicted on seismic data sets.

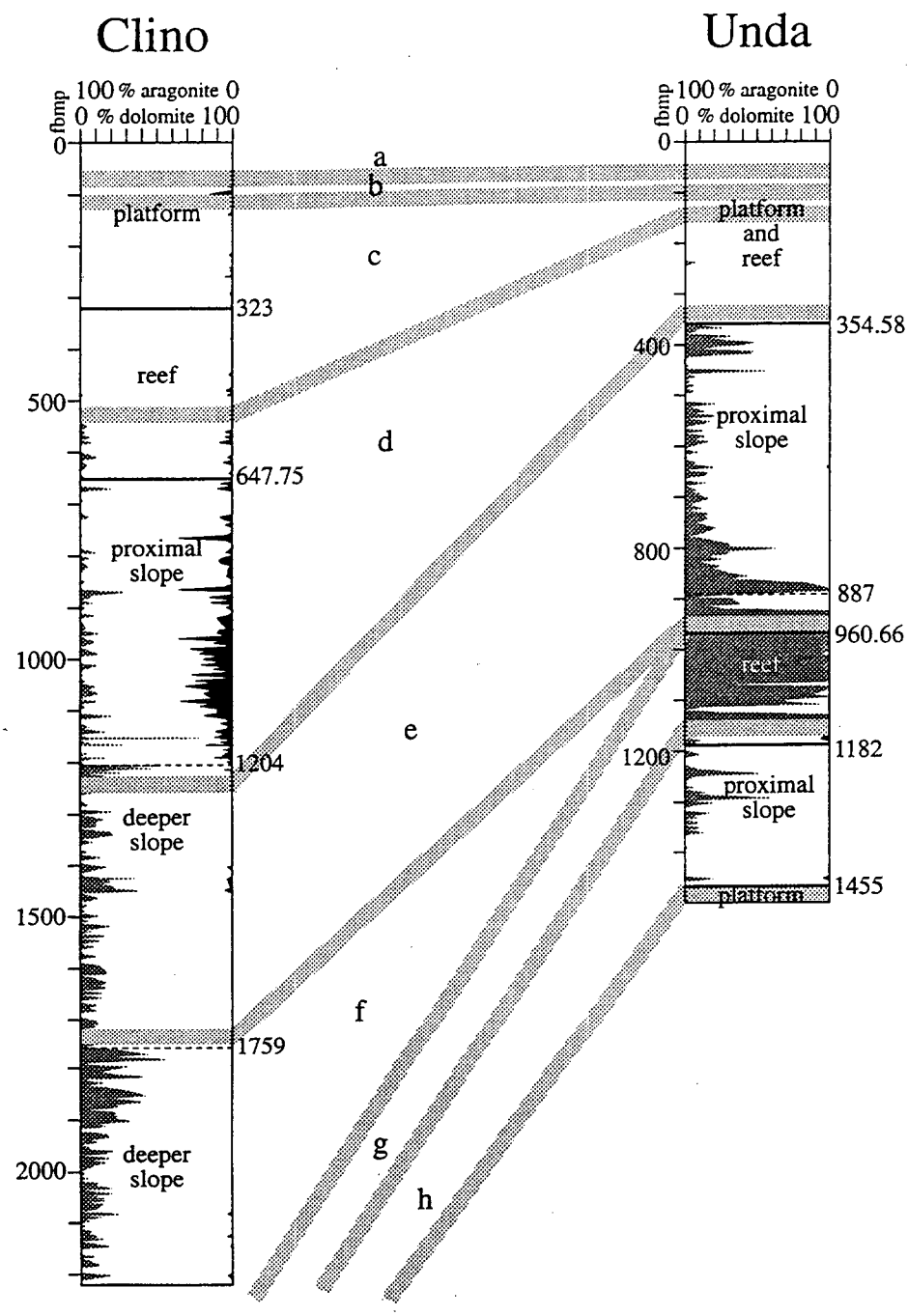

Figure 1: Correlation between seismic sequences and mineralogical content. Many sequence boundaries coincide with changes in mineralogy. Note also the increase of dolomite below several sequence boundaries.

GEOCHEMISTRY AND ORIGIN OF REGIONAL DOLOMITES

(DEFGO285ER13416)

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The major goal of this project is to better understand the conditions for the formation of ancient, massive dolostones occurring over regional scales within sedimentary sequences deposited in a range of settings. Lack of a modern analogue for ancient massive dolostones limits the application of the uniformitarian concept to developing models for the ancient regional dolostones. In addition it has not been possible to synthesize dolomite in the laboratory under conditions similar to the sedimentary or diagenetic environments in which the dolomites must have formed. The result of this is the strong reliance of the carbonate research community on ancient examples for understanding the orugins of regional dolostones. Recognizing this, we asked how we might better geochemically exploit ancient dolomites to better understand their origins. At the time of inception and development of our project, trace element and stable isotope geochemistry was widely applied to dolomites, however, our project was unusual in melding expertise in "hard rock" geochemistry (Hanson) with expertise in carbonate petrology (Meyers). Specifically, our philosophy was to apply geochemical approaches that had been highly successful in igneous and metamorphic petrology to carbonate diagenetic systems. We also recognized that successful application of geochemical approaches, especially new approaches, requires thorough petrographic and stratigraphic characterization of the diagenetic history of the studied unit.

The rocks we initially selected for a detailed petrographic and geochemical case study were the Mississippian (Osagean) Burlington-Keokuk Fms. of Iowa, Illinois and Missouri. We chose this because: it has a well known stratigraphy, there are extensive dolomites in subtidal shelf limestones, there is well defined cement and dolomite zonal stratigraphy, and it is similar to other porous and permeable shelf dolomites that are hydrocarbon reservoirs. Our plan from the beginning was to first apply our geochemical techniques to this sequence of rocks to evaluate their diagenetic history; and to then apply the approaches to sequences that have quite different tectono-sedimentary settings, including those that are oil-producing reservoirs. As a result the Burlington-Keokuk Fms. became a valuable natural laboratory for developing new geochemical approaches because of the wealth of petrographic and geochemical background data we have amassed. We then extended our work to Devonian, other Mississippian carbonates, and to Neogene carbonates.

Below are general summaries of some of our important results and conclusions:

1. The project has clearly demonstrated that carbonate petrologists need not be restricted to "traditional" geochemical approaches of stable isotopes and a few trace elements for diagenetic studies. Our project has applied and in some cases developed techniques for high precision analyses of microsamples (rather than solely whole rock) for Sr isotopes, REE, U, Pb, U and Pb isotopes, B and B isotopes, Na, Cl, F and sulfate.
2. The project has shown that high precision U-Pb dating can be accomplished on some U-enriched diagenetic phases, thus opening the door to the possibility of wider absolute dating of depositional ages and of diagenetic components in sedimentary rocks.

3. The quantitative modelling of simultaneous variations of isotopes and trace elements has proven extremely useful in constraining composition of dolomitizing fluids, differentiating mixing from water-rock interactions, identifying extraformational sources of chemical constituents and in some cases constraining their sources, in Sr isotope dating of Neogene strata and their diagenetic phases, and in assessing dolomite neomorphism.
4. Our case studies have confirmed that most massive dolomites involve several episodes of dolomitization, even in Neogene examples.
5. Our case studies have clearly shown that there is no single hydrologic/geochemical model that explains most massive dolomites. Instead they show that large relatively massive dolomite can be formed by subsurface brines (Burlington, Swan Hills Fms.), seawater evaporitic brines driven by sea surface circulation (Miocene of Spain), brackish groundwaters driven by mixing zone dynamics (Burlington, Seroe Domi Fms.), and relatively normal seawater driven by mixing zone circulation below the base of a fresh water lens (Devonian, W. Australia). This is important because there is a strong sentiment in the carbonate community that most massive dolomites are seawater dolomites.
6. Our case studies have shown that the scale and effects of dolomite recrystallization can be assessed through combined petrographic and geochemical approaches. They have shown that many dolomites have **not** been neomorphosed, and in some cases, pristine and neomorphosed dolomites can easily be differentiated, one of the clearest examples being the Burlington dolomites. This is important because there is a sentiment in the carbonate community that most ancient dolomites have been recrystallized and therefore geochemistry cannot be used to determine their origin.

We are winding down the petrogenetic studies of dolomite and in the future plan to emphasize the precise dating of the times of sedimentation and/or diagenesis using expertise developed in our studies to date. This is based on the results of John Hoff's successful dating of a pre-upper Permian unconformity in the Lisbourne Field, Alaska using the U-Pb method. We intend to develop techniques for radiometric dating of U-enriched carbonate paleosols (calcretes, caliches) formed at subaerial unconformities in carbonate and clastic rocks of Paleozoic and early Mesozoic age to pecisely date the time of sedimentation. Precise absolute ages for the times of sedimentation are required for almost all types of geological interpretations and correlations whether for academic or commercial purposes, because time is the framework for understanding geology. Sequence stratigraphy is currently being applied to most if not all modern stratigraphic analyses, including global correlations of sequences, and the development of presumed global sealevel curves. The Paleozoic and lower Mesozoic time scale is very poorly calibrated because of the scarcity of high-precision, biostratigraphically well constrained absolute age dates. Therefore, there is a real need to date biostratigraphic boundaries more precisely in early Mesozoic and Paleozoic sequences in order to test and improve the dating of the duration and correlations of sequences used in sequence stratigraphy.

Energy Flux and Hydrogeology of Thermal Anomalies in the Gulf of Mexico Sedimentary Basin - South Texas Example

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The Gulf of Mexico sedimentary Basin is perhaps North America's greatest energy resource locale, possessing large reserves of oil, natural gas, lignite, uranium, and geopressured/geothermal energy. Despite intensive oil and gas exploration, some of the basic scientific questions about the nature of the thermal and fluid pressure systems remain unaddressed, despite their relevancy to understanding the region's energy resources.. For instance, does either free or forced convection play a significant role in energy transport; what causes the bands of anomalously high temperatures; why does the thermal gradient increase with depth; and how long and where have excess fluid pressures existed? The objectives of this study are: 1) to evaluate if observed heat flow anomalies in the Gulf of Mexico sedimentary basin, if reconfirmed by extensive data analysis, can be accounted for by conduction alone or if convection is a significant perturbing factor; 2) to determine if the present potential field is amenable to convection hypotheses; and 3) to develop fluid and heat flux histories compatible with both compiled and newly collected data. In order to test the hypotheses posed to address these objectives, we compiled an extensive data base of fluid pressures, water chemistries, and formation temperatures from industrial data services, state well records, and the published literature; installed these data on a G.I.S for analysis; analyzed selected drill cores and cuttings for their mineralogy; obtained samples from which we measured thermal conductivity, radiogenic heat production, and porosity/bulk density; analyzed several major commercial and governmental computer codes for possible utilization; and written codes to simulate heat conduction and analyze the propensity for free convection. We are presently continuing to collect thermal property data; validating the temperature and pressure data to infer predevelopment conditions; calculating areal buoyancy gradients; and implementing a 2-D/3-D model to simulate the study area's temperatures and pressures.

Over 25,000 data points, reflecting basin pressures and temperatures at depths of up to nearly 5 kilometres (over 16,000 feet) have been compiled, and our analyses reconfirmed the thermal anomalies discerned from earlier, much smaller data bases. The pressure data revealed that petroleum production created significant depressurization which extends beyond the immediate petroleum reservoirs and which has implications for regional subsidence trends and in the analysis of predevelopment fluid potentials. The much more sparse water chemistry data revealed several areas with significant buoyancy gradients. Our measured thermal property data represent some of the first in the Gulf Coast. These data suggest that radiogenic heat production, although small, is not insignificant and should be accounted for in simulation models and that sandstone and muddy sandstone thermal conductivities correlate best with the quartz content and much less so with porosity. Most previous simulation models used empirical porosity functions to estimate thermal conductivity. The analysis of shale cuttings indicated significant shrinkage so that laboratory measurements of shale thermal conductivity, porosity, and bulk density may be suspect. Preliminary numerical modeling to date, which uses the real data as produced, indicate that convection is a significant factor in geological time, regional scale heat transport, unless highly unusual thermal conductivities can be documented.

Search for Evidence of Large Comet or Asteroid Impacts at Extinction Boundaries

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Extra-terrestrial objects (comets or asteroids) impacting the Earth are capable of leaving chemical signatures in the geological record indicating the impact event and implying their origin. The use of chemostratigraphy of the trace, minor and major elements at major extinction zones in the fossil record provides information concerning possible impacts for the 26-30 Ma frequency of massive extinctions. The purpose of this research project is to seek geochemical evidence in the fossil record for causes of mass extinction with special emphasis on major global events in the history of the earth.

The analytical approach to measure elemental abundances across extinction boundary horizons, other stratigraphic sequences, and impact materials has been neutron activation analysis. About 40 trace, minor and major elements are determined by the automated neutron activation system at the LANL Omega West Reactor. The platinum group elements (PGE), Ir, Au, Pt, Os, and Re, are determined by radiochemical neutron activation analysis. Samples are usually collected by over 60 colleagues and collaborators from around the world.

We have completed geochemical analyses on four new suspected Cretaceous-Tertiary (K-T) sections (Brazil, Guatamala, and North Dakota, and Wyoming) and samples from the oil well drilling from the suspected Chicxulub crater site in the Yucatán Peninsular, Mexico. Only weak Ir signals were found at the Brazilian and Guatamala sections. Only one Chicxulub sample, which may represent the basement material associated with the impact crater, showed a very weak iridium value. Other elemental similarities between the basement material and fireball layer may be evident but not strong. The Cenomanian-Turorian Extinction Interval (C-T) (92 Ma) was used to test the 26-30 Ma cyclic comet swarm corresponding to the major extinctions. We have completed chemostratigraphic analysis over 30 sites around the world. Locations where iridium anomalies predominant are found in the southern western interior of the US and Columbia SA. The iridium anomalies are absent in Europe and elsewhere for the C-T interval. A Czechoslovakian section recently analyzed showed no Ir enrichment as was the case in a suite in Poland. Explanation of the origin of this geochmical anomaly is more complex than the K-T event. Chemostratigraphic examination of sections for the Pre-Cambrian-Cambrian interval, the Ordivician-Silurian boundary, Late Eocene-Oligene boundary, Devonian-Carboniferous boundary, and Frasnian-Famennian boundary continues. Some of these sections indicates enrichments of iridium but the origin is not always clear. Unlike the K-T boundary where the iridium signal is sharp, the iridium in these key horizons are weaker and less defined.