

of the granulite. This difference accounts for the variation in ΔT between the two plutons and is considered the pressure-dependent parameter, assuming no differences in temperature. The geobarometer probably works because of a limited temperature range, oxygen fugacity, and composition of the final melts to crystallize from calcalkaline plutons. We suggest the Hammarstrom and Zen geobarometer can be used to determine depths of emplacement of calcalkaline plutons with an accuracy similar to geobarometers commonly applied to metamorphic rocks.

Geochemistry: Waters, Etc.
Room 301 Fri PM
Presider, T. Lutz, Univ. of Pennsylvania
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V52B-01 1330h
Carbon in Natural Goethites

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The content of carbon (reported as CO_2) in twenty natural goethites ($\alpha - FeO(OH)$) analyzed for this study ranges between 0.2 and 2.1 wt. percent. Most of this carbon is not phosphoric-acid extractable. The $\delta C-13$ values of the total carbon range between -30.7 and -12.8 per mil with a single value at -8.1 per mil.

Most of the natural goethites in this study contain nonstoichiometric water. The amount of aluminum in these samples is too small to attribute much of this excess water to clays. However, it is observed that there is a general correspondence between the amount of excess water in a goethite sample and the amount of carbon in the sample. A linear regression of the data points yields the expression: $X(\text{excess water}) = 2.1K(\text{carbon}) + 0.01$ with $r = 0.71$, where the X refers to mole fraction. The negative $\delta C-13$ values noted for the total carbon in these samples suggests that much of this carbon may be in organic molecules of biological origin. Such molecules would have a stoichiometric C/H ratio of about one, which does not account for all the excess water in these samples. A series of detailed dehydration-decarbonation experiments were performed on a goethite sample with a high content of carbon and excess water and a total carbon $\delta C-13$ value of -19.5 per mil. These experiments indicate that there are probably three isotopic carbon components in the sample: (1) "molecular CO_2 " trapped in the goethite structure, (2) carboxyl carbon, (3) "hydrocarbon". An inferred "reverse" $C-13$ fractionation between the hydrocarbon and carboxyl suggests that these molecules may be "organic acids" of biological origins. All these components appear to be trapped in the goethite. Consequently, carbon content and isotopic data may provide information on ancient environments of goethite formation.

V52B-02 1345h
Anglesite Solubilities in Water and Sodium Sulfate Solutions to 85°C

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To evaluate the stoichiometry and stability of lead sulfate complexes, the solubility of synthetic anglesite was measured at 25°, 40°, 55°, 70°, and 85°C in water and in 0.001, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 M Na_2SO_4 solutions. Experiments were conducted using a glass reaction vessel - water bath apparatus and anglesite solubilities, as dissolved lead, were determined using atomic absorption spectrometry. Equilibrium solubilities, obtained within 248 hours for all experimental conditions, ranged from 1.5 ppm at 25°C in 0.05 M Na_2SO_4 solutions to 31 ppm at 40°C in pure water. Two lead sulfate complexes were detected with stoichiometries described by the reactions:

(1) $Pb^{2+} + SO_4^{2-} = PbSO_4(aq)$
 (2) $Pb^{2+} + 2SO_4^{2-} = Pb(SO_4)_2$

Stability constants for these complexes were derived and are given as log K at each temperature in °C:

complex	25	40	55	70	85
$PbSO_4(aq)$	2.4	2.5	2.6	2.7	2.8
$Pb(SO_4)_2$	3.5	3.7	3.8	3.9	3.9

Traditionally, galena and lead chloride solubility techniques have been employed to study lead complexes. However, because of the relatively moderate stoichiometric solubility of lead sulfate and the weak nature of lead sulfate ion-pairs, solubility techniques using anglesite are more appropriate than galena and lead chloride methods for the study of many lead complexes of geochemical interest.

V52B-03 1400h
Ultrasonic Equation of State for Water and NaCl-water Solutions at High Pressure and Temperature

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The equation of state of water and NaCl-water solutions is an important starting point in thermochemical calculations of mineral stability and the solubility of various species in natural fluids. Most of the data available for determining the equation of state of water and NaCl-water solutions come from P-V-T measurements. Properties such as thermal expansion coefficient and compressibility are calculated from these data by taking temperature and pressure derivatives. The measurement of the velocity of ultrasound allows for a better determination of the equation of state since it provides a more direct measurement of the compressibility and can be made inherently more accurate and precise. We have made measurements of ultrasonic velocity in water and a 3.5% NaCl-water solution at pressures up to 0.7 GPa and temperatures up to 200°C. These measurements have been made possible by the design of a fluid cell which allows pressure to be transmitted to a reactive liquid sample through a flexible bellows. The cell prevents contamination of the fluid, and is virtually inert to the sample under the conditions of the run. Data collected to date show that water and NaCl-water solutions retain some of their anomalous properties at pressures up to at least 0.3 GPa. This method is much more sensitive to subtle changes in the compressibility at high pressures and temperatures than are P-V-T methods. Extension of the measurements to higher temperatures (and perhaps higher pressures) should provide theoretical geochemists with a better framework for calculations of solubilities and mineral equilibria under conditions appropriate for hydrothermal systems, ore deposition, metamorphism, and nuclear waste repositories. The apparatus can be used for a variety of electrolyte solutions and may even be adaptable to measurements on water-CO₂ solutions, and more complex systems.

V52B-04 1415h
Interface Controlled Disequilibrium Growth of Carbonate Solid-Solutions

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Experiments on calcite bicrystals which form (Ca,Sr)CO₃ solid-solutions by chemically induced grain boundary migration (CIGM) are influenced by the properties of the interface in the bicrystals.

3-D characterization of volume swept by the boundary shows Sr concentration from $1 - 4 \text{ mole}\%$ in the near surface swept area that decreases linearly to background level 130µm below the surface. Concentrations decrease as step functions to background levels at the original and final boundary positions, except where the boundary has reversed direction. In doubly swept areas, Sr is outside the area between the original and final boundary positions, and concentrations are higher at large depths below the surface.

Migration morphology is roughly repeatable on bicrystals with the same misorientation, but not for those with different misorientations. Migration distances tend to decrease with boundary misorientation. Very low angle boundaries (<2°) often do not migrate. Migration rates of 2µm/hr at about 0.65T_m were seen in situ in CIGM experiments in a heat stage, but are faster initially. Direction reversals were observed, and rapid initial growth rates were seen in situ for new grains nucleated at SrCO₃-CaCO₃ interfaces.

Dependence of the growth process on misorientation suggests interface structure affects the kinetics of solid-solution formation by a low temperature solid-state process. Spatial inhomogeneity of solute concentration, presence of step functions at the boundary, and near surface concentrations less than 1/8 equilibrium concentrations suggest that disequilibrium in chemical potential of cation solute may exist between the boundary and the crystal matrix. However, rapid initial migration rates suggest transient chemical potential gradients influence the kinetics of this process.

V52B-05 1430h
The Content of Natural Waters

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We have measured the ¹⁰Be concentration of various natural waters including: rain, Potomac River water, Appalachian Piedmont ground water, geothermal brines from the Cerro Prieto (Mexico) and the Salton Sea (California - USA) fields. These samples were filtered on a 0.2µm pore diameter membrane and we processed volumes ranging from 100 liters to 100 cc. The ¹⁰Be concentration varies from values below 10² to above 10⁴ atom/g. The highest concentration of

¹⁰Be in solution has been found in the Salton Sea geothermal waters that have the lowest pH and the highest salinity of all the samples. The concentration of ¹⁰Be in regolith solids (soil and sediments) with which these natural waters have reacted generally fall between 10³ and 10¹¹ atom/g. The differences in concentration of ¹⁰Be in solids and solutions is in accord with the very effective sorption and retention of this isotope by fine-grained surficial materials. These results suggest that ¹⁰Be behavior in vertical soil profiles fits mainly, a simple model combining ion exchange (with very high distribution coefficients for clays) and surface adsorption perhaps through hydrolysis. However, transport of measurable quantities of ¹⁰Be to depths of 10m or greater in soils may require other processes in addition to the poor solution transport inferred from our results on waters.

V52B-06 1445h
A Flow Through Apparatus for the Study of Rodinization

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Recent interest in low temperature (< 400°C) water/rock (W/R) interactions and the need for an experimental approach that more closely duplicates natural processes has led to the development of the flow through apparatus. To date most of the W/R interaction experiments have been performed in one or more types of closed agitated type hydrothermal equipment described by Seyfried et al. (1979). Such apparatus provides information on the steady state fluid chemistry; however, recent work (e.g.; Dibble & Potter, 1982) has concluded that many of these W/R interactions are kinetically controlled and are path dependent. The flow rate (hence W/R ratio) in the experimental system may play a major role in determining both chemistry of solution and paragenesis of secondary phases.

The flow through reaction system is effective in studying chemical and physical reactions occurring during open system-infiltration type fluid flow through porous media. The apparatus was developed to add to the existing Ti top gold cell of Seyfried et al. (1979). The gold cell is a 240 ml reservoir for the reacting solution which flows through a 3-13 cm gold tube filled with mineral or rock powders. The flow rate is computer controlled and ranges from 1-10 ml/day, and the effluent solution is sampled for chemical analysis without flow interruption. This system conforms to the basic requirements of a good experimental design: 1) inertness, 2) flexibility, and 3) ease of operation, and it enables flow through experiments to be conducted under inert conditions at temperatures of up to 400°C, fluid pressures to 1 kb, and flow velocities from several thousand to < 1 m/yr.

Several experiments have been performed at 300°C and 300 bars (P_{total}=P_{fluid}) using this flow through apparatus in order to study the chemical processes accompanying the formation of serpentinites, rodinities, and black wall assemblages. The chemical character of the effluent and extent of mineralization depend on flow rate, duration, and the compositions of initial fluids and solids. The effluent was sampled daily, measured for pH, and analyzed chemically. The experimental charges were sectioned and analyzed by XRD, SEM/EDAX, and electron microprobe to identify secondary minerals. The secondary growth includes serpentine minerals, clays, and hydrous calcite; the latter may be metastable precursors to rodinities. The fluids responsible for serpentinizing ultramafic rocks appear to be capable of rodinization and black wall mineralization.

V52B-07 1515h
An Evaluation of Absolute Carbon Concentrations Measured by the Beta Track Technique

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The poor agreement shown by carbon dioxide solubilities measured in diopside liquid by several methods has led to the speculation that absolute concentrations measured by the beta track technique are not accurate. Furthermore, carbon contents of 100 wt. ppm in olivine at 30 kb measured by Tingle et al., 1985 contrast with the 6.8 ppm value cited by Mysen et al., 1976, even though both studies employed the beta track technique. In order to constrain the possible explanations for the above discrepancies, two types of experiments have been conducted. First, calcite, synthesized from calcium oxide and carbon-14 labelled, silver oxalate, was equilibrated in the presence of vapor at 0.1 GPa 1040 C, 3.0 GPa 1040 C, and 3.0 GPa 1400 C to test the hypothesis of Rai et al., 1983 that 14/12 fractionation may explain the lower solubilities measured by the beta track method. Within experimental error, the grain densities recorded by the nuclear emulsions in identical exposure times are equivalent for the three specimens, thus demonstrating that 14/12 fractionation at elevated temperature is not significant on the time scale of the experiments. Second, single phase CO₂-undersaturated glasses were prepared from Amelia albite and the labelled silver oxalate at 2.0 GPa and 1450 C; the carbon concentration measured by the beta track method was compared to the amount of CO₂ sealed into the capsule. The scatter in these data suggest that absolute concentrations measured by the beta track technique may be subject to errors of 15% or greater. Some possible sources of error will be discussed.