

the sampling, such as poor visibility and strong bottom currents were overcome and samples of hydrothermal fluid, gas, rocks, and particulate matter were collected directly from the vent. Water samples and hydrothermal fluid were taken with a homemade 1 l cylindrical bottles of two lines by flushing in from the bottom for about ten minutes until total displacement of the seawater; similar procedure was carried out for gas samples. Particulate matter was collected with 0.4mm polycarbonate membrane filters and preserved in a desiccators at a fridge temperature until analysis onshore. Preliminary description of the rock samples suggest that pyritization is the main mineralization process. Filters containing hydrothermal particulate matter were surveyed under the scanning electron microscope in order to identify the nature (inorganic and organic), as well as the chemistry of the particles. SEM examination revealed the presence of particles of different kind that suggests high degree of mixing and re-suspension: Planctonic organisms and organic matter appeared to be abundant; 25 micron particles of different carbonate faces and inorganic particles of silicates were also recognized. Distinctive euhedral colloidal grains were identified as the resulting process of precipitation from the solution. Microanalysis of iron and sulfur content of 10 micron particles indicate a very likely sulphide mineral face (greigite); 8 micron cinnabar particles are consistent with the mineralization conditions, observed as well in the inner walls of the vent. Analyses of dissolved and particulate trace metals are still ongoing at labs in New Zealand and Mexico and will be incorporated in a near future.

V32A-0960 1330h POSTER

Contaminant Transformation by a Biogenic Manganese Oxide

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Biomining of manganese by *Pseudomonas putida* strain MnB1 produces tetravalent manganese oxides that surround the exterior of the bacterial cell. The manganese oxides produced by *P. putida* transform the herbicide atrazine, a widespread environmental contaminant, by dechlorination, dealkylation and demethylation reactions. The transformation reactions catalyzed by biogenic manganese oxide surfaces create a suite of transformation intermediates whose properties, such as aqueous solubility, toxicity and biodegradability, differ dramatically from those of the parent compound. The rates and products of atrazine transformation by biogenic manganese oxide surfaces were examined as functions of temperature and water potential. Air-dry samples of hydrous manganese oxide (δ -MnO₂) and biogenic manganese oxide were isotopically equilibrated to -3.10, -0.50 and -0.04 MPa at 40 degrees Celsius and to -0.04 MPa at 20 and 30 degrees Celsius. The concentrations of atrazine and eight transformation intermediates were determined by HPLC. Our results suggest that biogenic manganese oxides may contribute greatly to the detoxification and immobilization of organic contaminants in the environment because of their nanoparticle size, large surface area and high chemical reactivity.

V32B MC: Hall D Wednesday 1330h

Geomaterials: Melts and Fluids

Presiding: C Romano, University of Rome III

V32B-0961 1330h POSTER

A Natural Bonding Orbital (NBO) Analysis to Explaining the Effects of T-O-T Bond Angles on ²⁹Si and ²⁷Al NMR Chemical Shifts in Aluminosilicates

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It is recognized that ²⁹Si and ²⁷Al NMR chemical shifts in aluminosilicates or similar glasses have a clear correlation with the variation of T-O-T bond angle (T here as tetrahedral atom Si or Al atom). With the increasing of T-O-T bond angle, the ²⁹Si and ²⁷Al NMR

shielding values also increase. Detailed understanding of the nature of the relationship between the chemical shift and the distribution of T-O-T bond angles could potentially lead to important structural information for crystalline materials with complicated chemical environments and glasses with intrinsic disorder by providing insights into properties such as the Si/Al ratio, Si/Al ordering, and possible Al-O-Al linkages.

In order to determine a mechanistic explanation for this phenomenon from an electron structure viewpoint, high level ab initio NMR calculations were performed and compared with natural orbital bonding (NBO) analysis on a cluster model with different T-O-T bond angles. Based on the NBO analysis results, two factors may count for this correlation: 1) a slight increase of population of the Al-O and Si-O bonding orbital electrons and dramatic change of their electron distribution shapes (with more s orbital component and less bond bending) and 2) one of the lone pairs on O atom diffusing itself from the vicinity of O to the space close to Al or Si may also contribute more shielding to them. NBO analysis results also explained why there is no simple correlation between the T-O-T bond angle and ¹⁷O NMR chemical shift.

V32B-0962 1330h POSTER

New Measurements of the Densities of Copper- and Nickel-Sulfide Liquids and Preliminary Estimates of the Partial Molar Volumes of Cu, Ni, S and O

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We present the results of density measurements in Ni- and Cu-sulfide liquids. Density measurements were performed *in-situ* at 1250°C under controlled-atmosphere conditions using the modified single-bob (MSB) Archimedeon method. The MSB consists of a ~2 mm diameter rod with a ~6 mm long ~7 mm diameter cylindrical bob attached ~7 mm from the base of the rod. The bob and crucible were constructed from Yt stabilized zirconia to minimize reaction with the corrosive sulfide liquid. Zirconia density at temperature was calibrated against the known density of molten Cu metal (Drotning 1981, High Temp-High Press 13: 441-458). Density was determined by measuring buoyancy as a function of immersed volume. Buoyancy was measured with a 0.1 mg resolution analytical balance interfaced with a computer. The crucible is mounted on a micrometer "elevator" allowing regulation of immersion with .005 mm resolution. Temperature was measured with an S-type thermocouple in contact with the bottom of the crucible.

We explored log(f_{O_2}) from -8.2 to -12.6 and log(f_{S_2}) from -1.9 to -3.3. Five measurements have been made so far. Cu-sulfide densities range from 6.32 to 6.36 g/cc and were reproducible to $\pm 0.7\%$. Measured Ni-sulfide densities were lower, ranging from 5.27 to 5.79 g/cc. Wetting problems in Ni-sulfide compositions made these measurements more difficult. Reproducibility in Ni-sulfide melts was roughly $\pm 5\%$.

Measured density values were used to regress preliminary partial molar volumes of sulfide liquids in the Cu-Ni-S-O system. A linear least squares fit was derived from the five density measurements along with the densities of pure molten Cu (Drotning 1981, *ibid.*) and Ni (Nasch 1995, *Phys Chem Liq* 29: 43-58) at 1250°C. Melt compositions under experimental conditions were estimated using the thermodynamic model of Kress (submitted). The molar volume of the system (V) can be expressed as: $V = 8.18 X_{Cu} + 7.38 X_{Ni} + 30.33 X_S$ where X_i is the mole fraction of component i. Oxygen contents were too low to estimate the partial molar volume of this component.

V32B-0963 1330h POSTER

Densified SiO₂ glass: A Raman and XANES Oxygen K-edge spectroscopic study

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Vitreous SiO₂ continues to be one of the most commonly studied and well understood of all condensed amorphous phases. Not only is it of interest in the geosciences, particularly among petrologists and vulcanologists, but v-SiO₂ also serves as a common proving ground for physicists and chemists, both experimental and theoretical, in addition to being a major focus of research in the material sciences. Our interest in SiO₂ stems from its chemical and structural simplicity, as it is generally viewed as a three-dimensional framework of alternating Si⁴⁺ and O²⁻ ions in which tetrahedral SiO₄ units are linked by corner-shared oxygens forming a completely polymerized network. Limited by these criteria, at least over a moderate range of conditions, the structure of the glass can be relaxed at different pressures and temperatures by varying its distribution of intertetrahedral Si-O-Si angles. Its density (ca. 2.2 g/cm³) for the glass fused at ambient pressure can thus be considered a reflection of the Si-O-Si bond angle distribution, and perhaps also indicative of its ring statistics. Using Raman and X-ray Absorption Near Edge Structure (XANES) spectroscopy, we have characterized the structure of a series of glasses formed by isobaric quench from supercooled liquid temperatures as high as 8 GPa for which the density reaches 2.58 g/cm³. The most noticeable change in the Raman spectrum as a function of density is observed in the strong band centered near 400 cm⁻¹. This band becomes very narrow as it loses much of its intensity on its low frequency side. This observation can be interpreted as a change in the Si-O-Si angle distribution towards smaller angles. In accord with the low frequency behavior, we also observe a shift in the high frequency Si-O stretching bands to lower frequency. Non-bonded Si-Si repulsions are increased with narrower Si-O-Si angles, thereby lengthening the Si-O bonds and decreasing Si-O stretching frequencies. Changes in the oxygen K-edge are small in comparison to those observed in the Raman spectrum but it is possible to make correlations in order to interpret features in the XANES spectrum as they are related to glass structure. A complete understanding of how the structure of vitreous SiO₂ varies with pressure can help us understand how the properties of molten SiO₂ change with pressure and provide a foundation for our understanding of more complex silicate liquids at high pressure.

V32B-0964 1330h POSTER

Bonding Preferences of Non-Bridging Oxygens in Calcium Aluminosilicate Glass: Evidence from O-17 MAS and 3QMAS NMR on Calcium Aluminate Glass

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Non-bridging oxygens (NBOs) play a significant role in the thermodynamic and transport properties in glasses and silicate melts. Previous oxygen-17 (O-17) triple quantum magic angle spinning (3QMAS NMR) data have shown the presence of NBOs in several calcium aluminosilicate (CAS) glasses on the CaAl₂O₄-SiO₂ join (Stebbins and Xu 1997). The observed chemical shifts of these glasses are similar to those for the NBO in calcium silicate glasses (Stebbins et al. 1997 and Stebbins et al. 1999); however, a recent O-17 MAS NMR study of crystalline CaAl₂O₄ showed that the NBO peak in an associated impurity phase is shifted to a higher frequency by 30 to 40 ppm from that of CAS and Ca-silicate glasses (Stebbins et al. in press). This finding suggests that Si is the preferred network cation for NBOs in aluminosilicate glasses and melts at the glass transition temperature. The preference for Si over that of Al as the network cation host for NBOs has also been suggested by Raman and other spectroscopic techniques (Mysen 1988).

To investigate this apparent preference for Si-NBO, O-17 3QMAS and MAS experiments were conducted to examine the location of the NBO peak in the spectra of a calcium aluminate glass. Since the CaAl₂O₄ glass is difficult to make by conventional cooling methods, the binary eutectic composition (63CaO-37Al₂O₃) was chosen. The resulting O-17 MAS spectrum shows an intense, relatively narrow peak centered at 72 ppm, which nearly coincides with the peak location and width of the Al-O-Al peak in the crystalline Ca-aluminates (Stebbins et al. in press.) (70 ppm). There is a broader, less intense peak centered at 155 ppm that is assigned to the Al-NBO peak. This peak is in approximately the same location as that for a Ca-aluminate phase reported by Stebbins et al. (in press) (137 ppm). In addition, our 3QMAS data show that the peak maximum of the NBO in the Ca-aluminate (-85 and 150 ppm in isotropic and MAS dimensions, respectively) differs significantly from that of the calcium aluminosilicates and Ca-silicates of Stebbins et al. (1997 and 1999) (approximately -61 and 95 ppm in isotropic and MAS dimensions, respectively). Our data, when combined with previous data on CAS and CS glasses, strongly

suggests that most of the NBOs in calcium aluminosilicate glasses are bonded to Si, not Al.

V32B-0965 1330h POSTER

Fluorine-19 NMR Results on Crystalline Models for Fluoride Sites in Silicate and Aluminosilicate Glasses and Melts.

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As part of an ongoing effort to apply Fluorine-19 NMR to understanding the effects of fluoride on the structures and properties of silicate glasses and melts, the local environment of fluoride anions in several fluorosilicate and fluoroaluminate crystals and silicate glasses has been explored using F-19 MAS NMR. A compilation of this work with recent F-19 NMR chemical shift data has yielded several trends in the chemical shift. The chemical shift generally increases with the radius of the adjoining cation, which is qualitatively similar to the trends for oxygen anions in simple metal oxides and chlorine anions in crystalline chlorides. This effect was less pronounced in the fluoroaluminates and fluorosilicates (about 220 ppm from NaF to CsF versus about 60 ppm from Na₂SiF₆ to Cs₂SiF₆), implying that the strong bond to the Al or Si dominates the electron distribution around the fluorine anion. Another effect on the chemical shift was the coordination number of the fluorine, although it was difficult to establish a simple relationship between coordination number and chemical shift. In F-La(n) and F-Ca(n) sites (where "n" is the coordination number), increasing the coordination of the fluorine atom shifts the chemical shift to lower frequencies. In Na, Ca, and Ba fluoroaluminates, however, increasing coordination in Al-F-M(n) sites (where "M" is the coordinating cation) increases the chemical shift. The latter is also observed in Al-F-Al sites in Ba fluoroaluminates; as the number of coordinating Ba atoms increased, the position of peak maximum increased from -173 to -145.9 ppm. This may not have been due solely to the increasing coordination by Ba atoms, however, since the Al-F-Al bond angle decreases as the number of surrounding cations increases.

Using this compilation of crystalline model compound F-19 peak positions, we were able to analyze spectra for several silicate and aluminosilicate glasses and identify the coordination environments of the fluorine anions. The major feature in the barium silicate glass spectrum is a broad peak (at -19 ppm) near that of crystalline BaF₂ (-15 ppm). This implies that the Ba silicate glass contains a similar coordination environment as BaF₂ (F-Ba(4)) but with a range of bond lengths and, possibly, coordination numbers. A low intensity shoulder at -131 ppm was attributed to the structural unit Si-F-Ba(n) due to its proximity to the Si-F-Ba(2) site in crystalline BaSiF₆ (-112 ppm). The main feature in the Ba aluminosilicate glass overlapped the ranges for Al-F-Ba(n), Si-F-Ba(n), and Al-F-Al structural units, so assignment of this peak to a particular structural unit is impossible. However, it is possible to say that this glass has a minimal amount of F-Ba(n) structural units.

The studied Ca aluminosilicate glass contains a different fluorine environment than the Ba aluminosilicate. Our data for Ca aluminosilicate glass corroborates previous work on glasses of this composition, with the major feature of the spectrum (-152 ppm) within the observed range for Al-F-Ca(n) structural units (-143 to -154 ppm). There was also an unresolved shoulder centered at -126 ppm near the ranges of Si-F-Ca(n) (-123.4 to -134.5 ppm) and F-Ca(n) (-104 to -112.4 ppm) structural units. An additional intensity in the higher frequency spinning sidebands also suggests a considerable contribution from sites similar to those found in the Ca silicate glass (F-Ca(n) sites). The presence of F-M(n) sites in the Ca aluminosilicate but not in the Ba aluminosilicate suggests that the higher field strength cation can more effectively compete with Al cations for bonding with F anions. This supports previous conclusions about partial ordering of F anions around higher field strength cations.

V32B-0966 1330h POSTER

Ion-pair Formation and Ion Mobilities in Aqueous NaCl and KCl at High Temperatures from Conductance Data

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The electrical conductivity of aqueous solutions of NaCl have been measured at 651 K and 670 K at 28 MPa for molalities up to 1.0 mol/kg. These conductivities plus the results of Hwang et al.(1970), Ritzert and Franck (1968), and Mangold and Franck (1969) for aqueous KCl have been fit to the conductance equation of Turq, et al. (1995) with a consensus mixing rule and either mean spherical approximation or Debye - Hückel activity coefficients. Except at one state point, where the Coulomb interactions are the strongest ($\beta^* = \frac{e^2}{4\pi\epsilon_0\epsilon_r kT a} = 17.8$, where ϵ and a are the dielectric constant of water and the closest distance of ions approach, respectively), the simplest model that fits the experimental results reasonably well (2-3 %) at molalities up to 4.5 moles/kg is one with only the limiting equivalent conductance and a pair association constant adjusted. Activity coefficients calculated with either the MSA and ionic diameters or with the Debye-Hückel equation of Oelkers and Helgeson (with no salting-out) can be used with similar accuracy. At high concentrations this model predicts strong redissociation of the ion pairs which form at low concentrations.

The cluster model of Laria, et al.(1990) for the restricted primitive model is consistent with the qualitative predictions of our preferred model of pair association only. The model of Oelkers and Helgeson (1993) with substantial multi-ion association (triplets and quartets) does not fit the data without the physically unrealistic salting out coefficient so this model is not recommended.

For the state point with the highest betastarr (NaCl at 670 K and 28 MPa), more complex models are needed at concentrations above 0.05 mol/kg. Good fits to the data were found for multi-ion association models (5 adjustable parameters) and reasonable fits were found with only pair association and more complex activity models (4 adjustable parameters) so that the models are about equally accurate at equal complexities for this solution.

V32B-0967 1330h POSTER

A Truncated Virial Equation of State for Components of Hydrothermal/Magmatic Fluids

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The simplest equation of state (EoS) for components of hydrothermal/magmatic fluids is the ideal gas EoS, given by $PV/RT=1$, where P stands for pressure, V designates the molar volume of a fluid, T is the temperature and R represents the gas constant. This approximation can be used only at low fluid pressures (densities). The next universal and theoretically sound EoS is the virial equation of state truncated at the second virial coefficient, given by $PV/RT=1+B_m/V$, where B_m designates the second virial coefficient of a mixture. Importantly, the composition dependence of B_m is rigorously given by $B_m=\sum_i \sum_j X_i X_j B_{ij}$, where B_{ij} designates the second virial coefficient between (like or unlike) interacting components of a mixture, X stands for the mole fraction of a components of the mixture. This truncated virial EoS may be used at low to moderate densities of a fluid, corresponding to maximum pressures ranging from approximately 30 MPa at 700 K to 100 MPa at 1200 K. Fugacities of the components of hydrothermal/magmatic fluids can be calculated provided that the second virial coefficients B_{ij} are known. Virial coefficients are known or can be reliably estimated for many pure gases. The lack of information about cross virial coefficients for interactions involving water is the biggest obstacle to applying the truncated virial EoS to petrological problems.

We have compiled literature data and in many cases evaluated second cross virial coefficients from various types of experimental information: PVTX properties of gaseous mixtures; excess molar enthalpies of gaseous mixtures, and solubilities of water/ice in compressed gases. In all, results for 27 compounds are obtained, including hydrocarbons, alcohols, nonpolar and polar inorganic solutes. These data form a basis for development of empirical ways to estimate the mixture's interaction parameters of the popular Tsonopoulos and Hayden-O'Connell correlations, which employ the principle of corresponding states to predict the values of virial coefficients. A group contribution method to estimate second cross virial coefficients between water and organic compounds is discussed and recommended for interactions where no experimental data are available.

V32B-0968 1330h POSTER

An Experimental Study of Magnetite Solubility as a Function of Pressure Along the Dewpoint Curve in the NaCl-, KCl-, HCl-H₂O-Melt System.

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Magnetite (Mt) is a ubiquitous phase in magmatic-hydrothermal ore deposits and, thus, any model which aims to predict the evolving physical chemistry of porphyry-ore deposit environments must incorporate data on the equilibria that control the precipitation of Mt in such systems. Extant experimental data indicate that Mt solubility is controlled via the equilibrium $Fe_3O_4^{Mt} + 6HCl^V + H_2^V = 3FeCl_2^V + 4H_2O^V$ (Chou and Eugster, 1977, AJS, p 1296); however their experiments were performed at T=500-650°C by equilibrating Mt with a HCl-bearing supercritical aqueous fluid (NaCl-, KCl-free). Conversely, data from some natural Fe-bearing fluid inclusions have evinced that initial temperatures of magmatic volatile phases (MVP) in magmatic-hydrothermal environments may exceed 800°C, possibly even approaching 900°C, in the presence of melt (Clark and Arancibia, 1995, Giant Ore Deposits-II Conference, p. 511). Thus, there currently are no data constraining Mt solubility in the high-temperature regime obtained in natural magmatic systems. Additionally, there are no data on Mt solubility as a function of changes in the chemistry of the MVP. In the system NaCl-H₂O, the composition and, thus, the density of brine-saturated vapor change significantly as a function of pressure along a given isotherm and the components KCl and HCl act to shift the limbs of the solvi (Bodnar et al., 1985, GCA, p 1861; Anderko and Pitzer, 1993, GCA, p 1657; Shinohara and Fujimoto, 1994, GCA, p 4857). The absence of data constraining Mt solubility as a function of pressure along a given isotherm, the resultant change in composition and density, as well as deviations in the Na:K:H ratio of the MVP hinder the development of forward models of magmatic-hydrothermal systems. In order to provide these critical data constraining Mt solubility in geologically reasonable magmatic systems we have performed a set of experiments as a function of pressure in the vapor-only field near the 800°C isotherm in the NaCl-H₂O system. Natural Mt ($a_{Fe_3O_4} \sim 1$), a synthetic haplogranitic minimum melt (100 MPa) and an aqueous phase (molar K:Na:H=1) were reacted in Au capsules in rapid-quench Stellite-25 vessels, using water as the pressure medium, at 800°C, $\log f_{O_2}$ controlled by the NNO buffer, pressures of 100 and 120 MPa, and aqueous salinities of 1.8 and 3.0 wt. % NaCl equivalent, respectively. In all experiments the mass ratio of Mt:melt:fluid was 1:1:4. Detailed petrographic examination of run products did not reveal the presence of brine inclusions; however, fluid inclusions do contain opaque phases. Using the newly determined m_{FeCl_2} (0.0345 at 100 MPa and 0.0359 at 120 MPa) and m_{HCl} (0.0769 at 100 MPa and 0.0947 at 120 MPa) in the quenched MVP and the known fugacities of H₂O ($\gamma=1$) and H₂ ($\gamma=1$) at P and T, apparent equilibrium constants were calculated as $\log K = (C_{FeCl_2})^3 \times (f_{H_2O})^4 \div (C_{HCl})^6 \times f_{H_2}$. The values of log K are 1.605 at 100 MPa and 13.01 at 120 MPa. K is fixed for a given P and T except for the effect of activity coefficients for HCl and FeCl₂. The values of log K obtained in this study will facilitate more detailed characterization of the chemistry of magmatic-hydrothermal MVPs; both fossil MVPs and those that obtain in modern geothermal reservoirs. Determination of P, T, f_{H_2} and m_{FeCl_2} in fluid inclusions will allow for the direct calculation of a model HCl concentration in the MVP.

V32B-0969 1330h POSTER

Albite-Paragonite-Quartz Solubility: Experimental Constraints on the Thermodynamic Behavior of Si, Al, and Na in Aqueous Fluids at 0.5-1.0 GPa from 350-500C

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The solubility silica, sodium, and aluminum was measured under subduction zone conditions through experiments in pure H₂O and S-bearing solutions in equilibrium with albite-paragonite-quartz at 350-500C, 0.5-1.0 GPa in a piston-cylinder apparatus (sulfur was included for another study, and has no impact on measured solubilities). Starting materials were natural

Amelia albite, Brazilian quartz, and microcrystalline paragonite synthesized from finely ground Amelia albite, Al_2O_3 and H_2O at 0.5GPa and 400C for 138 hours. Solutions were extracted in 5% HNO_3 and analyzed by ICP-AES. Silica is the most soluble element (30 to 217 milli-molal), followed by sodium (9 to 108 milli-molal), and then aluminum (3-40 milli-molal). The results agree well with experimental trends of Woodland and Walther (1987, GCA, v. 51, p.365) and with the predicted values at 0.5 GPa calculated using SUPCRT92. Na-Al complexing were not required by the measured concentrations. Comparison with the results of Manning (1994, GCA v.58, p. 4831) and Woodland and Walther (1987) indicate that the solubilities of Si, Na, and Al increase sharply with increasing pressures and more moderately at higher pressures. These results provide the first measurements of alkali-silica-aluminum solubilities under high pressure conditions. The solubilities measured demonstrate that sodium, and by inference other alkalis, are very soluble at high pressures. Aluminum is also extremely soluble. Pressure enhances the solubilities of major rock-forming elements in pure H_2O . This indicates that metamorphic and subduction zone fluids can profoundly metasomatize the rocks they interact with as they migrate toward the surface.

V32B-0970 1330h POSTER

Experimental Determination of Calcite Solubility in H_2O -NaCl Solutions at Deep Crust/Upper Mantle Conditions: Implications for Metasomatism in Shear Zones

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The solubility of calcite in H_2O -NaCl solutions was determined by a weight loss method to halite saturation at 10 kbar, 600-900 °C, and at $X_{\text{NaCl}}=0.3$ at 6-14 kbar, 700 °C. Cleavage rhombs of pure natural calcite were encased in an inner Pt capsule, perforated to allow fluid access, and placed with salt solution in a welded outer Pt capsule. Experiments were conducted in a 1.91 cm diameter piston-cylinder apparatus with NaCl pressure medium, graphite heater sleeve, and W3%Rh-W25%Rh thermocouples.

At 800 °C and 10 kbar there is a very large salting-in effect, such that calcite at halite saturation is more than 40 times more soluble than in pure H_2O . CaCO_3 molality (mol/kg H_2O , m_{CC}) is proportional to the square of the NaCl mole fraction: $m_{\text{CC}} = 0.113 + 11.458(X_{\text{NaCl}})^2$. This implies that the solution-enhancing mechanism is the reaction of one mole of calcite with two moles of solute NaCl. There is also a strong increase of solubility with temperature in concentrated salt solutions: m_{CC} increases from 0.25 to 3.0 between 600 and 900 °C at 10 kbar. Increasing pressure from 6 to 14 kbar at 700 °C and $X_{\text{NaCl}}=0.3$ has a much smaller effect on calcite solubility.

Concentrated brines seem uniquely capable of explaining the great carbonate-alkali-metasomatized, high-temperature shear zones, such as the Attur Valley of South India (Wickham et al., 1994, J. Geol., 102, 379) and similar zones in South Norway, Queensland, Egypt, and Tajikistan. In these localities, carbonates with mantle-like stable isotope ratios have replaced crustal rocks in tracts as large as 100×10 km by up to 20% as veins and by pervasive metasomatism. Carbonate-rich concentrated brines formed at near-magmatic temperatures during deep-seated alkalic magmatism will deposit their carbonate load almost quantitatively upon cooling 200-300 °C in the deep crust.

V32B-0971 1330h POSTER

Hydration of carbonate-bearing species: Structure of aqueous CO_2 , HCO_3^- , and CO_3^{2-} from molecular dynamics computer simulations

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The hydration structure of carbonate species cannot be easily studied experimentally by conventional X-ray and EXAFS methods due to the fact that C and O atoms of the solute species are not distinguishable from O atoms of solvent water. This makes molecular computer simulations an especially promising alternative approach to understanding the structure of aqueous carbonate solutions. We have performed molecular

dynamics simulations of 0.5m Na_2CO_3 and 0.5m and 1.5m NaHCO_3 aqueous solutions, as well as H_2O - CO_2 -NaCl solutions over a geochemically relevant range of temperatures, pressures, and concentrations. While most of the MD simulations modeled the equilibrium hydration properties of the solutes on the time scale of 50-100ps, some of the simulation runs were particularly long (up to 2 ns) in order to effectively probe the structure and dynamics of long-lived ionic clusters of Na^+ and CO_3^{2-} formed in the solution. Due to the ion pair formation, the diffusion rates of both Na^+ and CO_3^{2-} ions in the Na_2CO_3 solution are ~ 3 -6 times lower than in similar chloride solutions, while the diffusion rate of HCO_3^- is about the same as that of Cl^- . The analysis of the solute hydration structure in terms of O-O and O-H radial distribution functions indicates that the negatively charged O atoms (O_c) of carbonate ions are hydrated by water molecules (O_w and H_w) in a manner similar to H_2O molecules themselves. Strong $g_{\text{OH}}(R)$ peaks at ~ 1.8 Å and $g_{\text{OO}}(R)$ maxima at ~ 4.5 Å indicate a high degree of hydrogen bonding around O_c . The hydration shells of carbonate and bicarbonate ions both contain 10 H_2O molecules, but the carbonate one is more structured due to the higher anion charge. In dense CO_2 -rich fluids, dissolved water molecules exhibit a high degree of H-bonding and form relatively stable H-bonded clusters. In contrast, CO_2 molecules dissolved in water-rich fluids are found in clathrate-like cages formed by surrounding H-bonded water molecules. This structural arrangement results in about tenfold decrease of the CO_2 diffusion rate in the H_2O -rich phase, compared to the CO_2 -rich phase under similar thermodynamic conditions.

V32B-0972 1330h POSTER

The Solubility of Calcite in H_2O at 5-16 Kbar and 500-800 °C

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The solubility of calcite in H_2O was measured at 5-16 kbar, 500-800 °C, using a piston-cylinder apparatus. The solubility was determined by the loss in weight of single crystals and by ICP-AES analysis of quench fluid. Calcite dissolves congruently at all conditions investigated. At 10 kbar, calcite solubility increases with increasing temperature from 1.57×10^{-2} molal at 500 °C to 5.70×10^{-2} molal at 750 °C. Comparison with previous work at lower pressures shows that the pressure dependence of calcite solubility is greatest between 1 and 5 kbar, where it increases at 500 °C from 1.80×10^{-5} molal (1 kbar) to 2.63×10^{-2} molal (5 kbar). The carbon species CO_2, aq predominates by >94% over HCO_3^- . Calcite solubility depends more strongly on pressure and temperature than predicted by existing thermodynamic data. This leads to higher standard molal enthalpy (127.39 kJ/mol) and entropy (330 J/mol K) at 10 kbar for the reaction $\text{Calcite} + 2\text{H}^+ = \text{Ca}^{2+} + \text{CO}_2, \text{aq} + \text{H}_2\text{O}$ than are predicted from existing thermodynamic data. Over the temperature and pressure range investigated, the solubility of calcite in pure water can be described by the equation: $\log m_{\text{Ca}} = -3.0323 + 0.0021475T + (25.227 - 0.02754T) \log \rho_{\text{H}_2\text{O}}$, where m_{Ca} is the Ca molality in solution, $\rho_{\text{H}_2\text{O}}$ is the density of H_2O in g/cm^3 , and T is temperature in °C. This equation can be used to model the composition of water-rich fluids evolved from metamorphic reactions involving calcite. Due to the strong pressure dependence of calcite solubility below 5 kbar, decompression of these evolved fluids will result in precipitation of most of the dissolved calcite load between 9 and 15 km depth.

V32B-0973 1330h POSTER

Aqueous Mercury-Sulfur and Gold-Sulfur Complexes: An In-situ EXAFS Study

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Mineral and ore formation processes which involve mercury or gold often depend on aqueous speciation of these metals, and bioavailability of mercury is also

affected by aqueous complexes. The nature of coordination by sulfur of these metals in aqueous solution is important for understanding the geochemical behaviour of these metals. The principal difficulty in using spectroscopy to study these heavy metal-sulfur complexes is that dissolved concentrations in sulfidic natural waters are very low. However, it is well known that Hg(II) is soluble in high sulfide concentrations and that Au(I) forms aqueous complexes with thiosulfate. Au(I) thio-sulfate complexes have been proposed as sources of secondary enrichment of gold in supergene environments (Webster and Mann, 1984).

We exploit these sulfur complexes to determine metal-sulfur bond distances and coordination numbers in aqueous solution. An internally heated titanium spectroscopic cell was designed for experiments on the high X-ray flux dynamic focussing EXAFS Station 16.5 at the Daresbury Synchrotron. Gold thio-sulfate solutions (10 mM) were prepared from sodium bis(thiosulfate) aurate(I) dihydrate. Mercury sulfide solutions were prepared by dissolving metacinnabar in 50 mM Na_2S solutions. X-ray fluorescence spectroscopic measurements were taken over the Au L(III)-edge at 11.918 keV and the Hg L(III)-edge at 12.284 keV to obtain the extended X-ray absorption fine structure (EXAFS) data.

At room temperature, the best fit to EXAFS experimental data gives Au(I) coordinated by two S's at 2.30 Å. No significant changes in Au-S distance are observed upon heating to 75 °C. Above 100 °C, the gold-thiosulfate complex decomposes. Au-S distances in the gold thiosulfate salt obtained from EXAFS are 2.28 Å. Hg is also coordinated by 2 S's at 2.30 Å at room temperature and at 75 °C in the aqueous solution examined. These bond distances are shorter than Hg coordinated by 2 S's in cinnabar, 2.368 Å, and much shorter than Hg coordinated by 4 S's in metacinnabar, 2.535 Å [distances here from X-ray diffraction data]. These experimental results provide new data suitable for refining computational models of metal-sulfur complexes, and enhance our understanding of the aqueous sulfur geochemistry of mercury and gold.

Reference:

Webster JG and Mann AW (1984) The influence of climate, geomorphology and primary geology on the supergene migration of gold and silver. J. Geochem. Explor. 22, 21-42.

V32B-0974 1330h POSTER

An Experimental Approach to CO_2 Sequestration in Saline Aquifers: Application to Paradox Valley, CO

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As part of a Bureau of Reclamation program to decrease the salt load of the lower Colorado River Paradox, Valley Brine (PVB) is being disposed of into the Leadville Formation via a deep-injection well, situated in southwest Colorado. A complex pre-injection process uses nano-filtration to minimize well-plugging scaling caused by elevated downhole temperatures and pressures. We address here the possibility of liquid carbon dioxide as an additive to the injection fluid in an attempt to increase formation porosity. We report here the CO_2 solubility results of preliminary experiments on pure water and PVB.

We used fixed-volume titanium and flexible gold-cell technology to (1) measure the solubility of CO_2 in PVB from surface to downhole conditions and (2) investigate the geochemical interactions between CO_2 -charged PVB and rocks from the Leadville Limestone. The apparatus is applicable to the general study of CO_2 sequestration in deep-saline aquifers where the understanding of the interaction of CO_2 -charged fluids and potential host rocks is important. The experimental procedure is an adaptation of the technology designed to study hydrothermal systems where seawater was reacted with basaltic rocks at high temperature and pressure. This procedure has been used extensively for the investigation of rock-water interactions and the determination of the solubilities of Na-K-Ca-Cl solutions over a wide range of temperature, pressure, and composition, along the vapor pressure curve and from beyond the critical point to the triple point.

To validate the experimental design we calibrated the system with published data on the binary CO_2 -pure water system. We obtained new data on the solubility of CO_2 in pure water and PVB ($\sim 21\%$ TDS) at 21 °C and 50 °C from 100 to 600 bars. At 21 °C the solubility of CO_2 (as wt% CO_2/g fluid) in PVB is 2.2, 2.3, and 2.6 at 100, 300 and 600 bars pressure respectively contrasted with 6.5, 7.4 and 8.5 in pure water at similar pressures. At 50 °C and the same pressures the solubility of CO_2 in PVB is 1.9, 2.1, and 2.5 respectively. Pressure/solubility relations suggest that differences between the solubility of CO_2 in pure water and PVB are not due to simple salting out effects. Experiments are underway to test a pure NaCl solution as an analog for PVB.

V32B-0975 1330h POSTER

A Technique for Determining Methane Hydrate Stability Limits Based on Raman Analysis of Synthetic Fluid Inclusions

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Methane hydrate is a naturally-occurring ice-like compound that is stable at low temperatures and high pressures. During the past decade interest in the occurrence and properties of natural gas (methane) hydrates has increased significantly owing to its potential as an energy source, its potential effects on current and past climates, as an agent of submarine erosion and as a hazard to ocean-going ships.

To better understand the properties of methane hydrates, a technique was developed which allows the P-T limits of the hydrate phase to be determined accurately and unambiguously. Synthetic fluid inclusions containing known concentrations of methane and water were prepared by loading measured amounts of water and aluminum carbide into platinum capsules, along with a fractured quartz core. The aluminum carbide reacts with water to form methane plus aluminum oxide. The capsules were placed into cold-seal bombs to heal fractures in the quartz to produce synthetic fluid inclusions. The resulting inclusions were examined on a microscope heating/cooling stage, and the temperature at which the methane hydrate phase dissociates was determined optically. Then, the same fluid inclusion was analyzed by Raman spectroscopy at this same temperature to determine the position of the C-H symmetric stretching band. The position of this band varies systematically with pressure. Using the pressure peak position calibration determined using a high pressure cell on the Raman microprobe, the methane pressure corresponding to the measured peak position was calculated. Using this technique, methane hydrate stability in pure water and aqueous salt solutions has been determined to pressures of approximately 400 bars.

The P-T limits of methane hydrate stability in pure water determined in this study are in good agreement with published values. However, results obtained for hydrate stability in the presence of 5, 10 and 20 weight percent NaCl aqueous solutions show poorer agreement with published data. Specifically, pressures obtained using the synthetic fluid inclusion Raman technique are generally higher than those obtained with other techniques. These differences may reflect failure to obtain equilibrium in some earlier studies, owing to the sluggish nature of the hydrate dissociation reaction.

V32B-0976 1330h POSTER

Barite Dissolution Rates Derived From Vertical Scanning Interferometry: A Comparison Between VSI and AFM

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Barite (BaSO₄) occurs naturally in many environments including crustal rocks, hydrothermal deposits, and marine sediments, and is sparingly soluble in aqueous fluids. Barite scaling in oil reservoirs and drill pipes is a common problem associated with extraction of heavy hydrocarbons. Waters used for volume replacement during the extraction process, can interact with barium in the reservoir and precipitate barite that obstructs flow and reduces oil recovery. Chelating agents such as EDTA are commonly used to keep barium ion in solution by complexing with it, effectively controlling the amount of barium able to react with the sulfate anion in solution. With a sound understanding of the dissolution/precipitation kinetics, the amount of chelating agent used by the oil industry can be minimized. This will help keep costs down during pumping, and reduce the amount of environmental contaminants needed for the process.

Most available data on barite dissolution rate have been collected using Atomic Force Microscopy (AFM). AFM provides excellent resolution of the mineral surface during dissolution; however, this excellent resolution comes at the cost of a narrow field of view. This project will provide a comparison between vertical scanning interferometry (VSI) and AFM. VSI is a relatively new technique in the field of Geochemistry. VSI can be used to measure retreat normal to the mineral surface. Because VSI offers a larger field of view, the amount of material removed can be integrated over a larger surface area, thereby averaging out inhomogeneities that might exist on the scale of AFM observations. VSI will provide information that will augment the current AFM data to allow a more complete understanding of barite dissolution.

This project involves measuring surface retreat on a freshly cleaved barite surface during treatment

with aqueous solutions with variable concentrations of EDTA over temperature ranges of 25-80°C. This study will generate dissolution rates from the barite surface to compare with those found through the use of AFM. This study will also look for trends in etch pit morphology on a larger scale and compare it to trends found using AFM.

V32B-0977 1330h POSTER

Rates of Mineral Dissolution Under Hydrothermal Alteration

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The significant gap between field and experimental rate estimations, attributed to the use of single minerals during experimental evaluation, makes controversial the evaluation of alteration budget in natural conditions. We propose an original approach to evaluate, simultaneously, the dissolution rate of K-feldspar, biotite and plagioclase during experimental alteration of granite rock by fluids having an initial composition close to the saturation with neogenic phases. The technique based on the isotopic doping technique is suitable for granite where minerals have different strontium isotopic signature and Rb/K ratio. Experiments were carried out at different temperature (i.e. 80°, 120°, 180°C) spiking the initial fluid composition in the less abundant isotope K and Sr isotopes (i.e. 39, 84 respectively) and following the evolution of the chemical and isotopic composition for 1 year. We demonstrate that the complex water-rock processes can be experimentally represented by an isotopic mixing proportion between the dissolving minerals and spiked solution from the first days of reaction. We have found that the (87Sr/86Sr) and (Rb/39K) dissolved rock end members do not change significantly in the range of temperature investigated in this study allowing to calculate the proportion of dissolved mineral, assuming the mass conservation law and the mixing isotopic equations for the system. Rates of mineral dissolution were, thus, estimated assuming the isotopic equilibrium of (41K/39K) ratio between fluids and neogenic phases precipitated during the interaction and the constancy of the surface area. Irrespective of the temperature we have found that the dissolution rate of plagioclase is only one order of magnitude higher than biotite and orthoclase. Since the constancy of the mineral dissolution rates with temperature, we propose that the strontium isotopic composition of natural hydrothermal fluids depends mainly on mineral proportion abundance and age of the granite rock.

V32C MC: Hall D Wednesday 1330h

Ultra High Pressure Petrology

Presiding: E Walsh, University of California

V32C-0978 1330h POSTER

P-T Estimates For Phengite-Kyanite Uhp Eclogites From A Highway Roadcut Near The Qinglong Mountains, Eastern China

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Recent highway construction across the Qinglong Mountains in Donghai, eastern China has exposed a 660 m section of gneiss, eclogite, and minor quartzite. The outcrop consists of steeply SE-dipping layers cut by several high-angle (normal?) faults. Eclogite layers are concordant with gneissic rocks and minor quartzites; a few discordant eclogite contacts appear to be intrusive. Most eclogites are characterized by abundant hydrous phases including talc, phengite, and epidote; many also contain kyanite. Inclusions of quartz aggregates after

coesite were identified in garnet and kyanite of both eclogites and quartzites, consistent with the reported occurrences of inclusions of coesite and coesite pseudomorphs in epidote and kyanite from both eclogite and quartzite, of this region (Zhang et al. 1995). Peak conditions of 3.0-3.5 GPa and 600-750°C were estimated using the thermobarometer of Ravna and Terry (2001) and the data set of Holland and Powell (1998). The Qinglong Mountains contain a variety of UHP eclogites, and are the classic locality for negative $\delta^{18}\text{O}$ values (-14 to 16‰/‰) for UHP minerals in eclogites, quartzites and surrounding gneisses (Yui et al. 1994; Rumble and Yui 1998) indicating that fluid may have been absent during peak-stage metamorphism.

V32C-0979 1330h POSTER

Northern Qaidam Caledonian UHP Terrane A New Discovery

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Several new Alpine-type HP/UHP terranes occur in the Altun-Qaidam-Mountains and Beishan of NW China; we have identified UHP garnet lherzolite and eclogite in the North Qaidam Mountains. This finding is supported by Raman spectrum identification of coesite inclusions in zircon separates from paragneissic rocks in the eastern part of the North Qaidam belt (Dulan region). Eclogite and garnet peridotite bodies of various sizes occur as blocks and layers in the Upper Proterozoic sequence of gneiss, amphibolite, marble, and schist. Comparable rocks have been identified from east to west in the Dulan, Xitianshan, and Da Qaidam areas, constituting an EW-trending belt over 350 km long, and from a few to Several new Alpine-type HP/UHP terranes occur in the Altun-Qaidam-Mountains and Beishan of NW China; we have identified UHP garnet lherzolite and eclogite in the North Qaidam Mountains. This finding is supported by Raman spectrum identification of coesite inclusions in zircon separates from paragneissic rocks in the eastern part of the North Qaidam belt (Dulan region). Eclogite and garnet peridotite bodies of various sizes occur as blocks and layers in the Upper Proterozoic sequence of gneiss, amphibolite, marble, and schist. Comparable rocks have been identified from east to west in the Dulan, Xitianshan, and Da Qaidam areas, constituting an EW-trending belt over 350 km long, and from a few to 10+ km in width. Most eclogite blocks are small (< 10 x 20 m), but few are up to 0.5 km². Eclogites in the Dulan area consist mainly of Grt + Omp + Phe (Si = 3.45) + Rt, with calculated P-T conditions of T = 624 - 735°C and P = 3.0 ± 0.2 GPa. Associated garnet peridotite P-T estimates are 837°C and 2.5 GPa. The enclosing gneissic rocks consist of Qz + Fsp + Bi + Hb ± Grt; the occurrence of coesite inclusions in zircon indicate in-situ UHP metamorphism. U-Pb dating of zircons from the Da Qaidam eclogite yields 495 Ma, consistent with new SHRIMP U-Pb dating of 443-495 Ma and Sm-Nd dating of 496 Ma for eclogite, suggesting that the UHP metamorphism of the North Qaidam terrane occurred in Early Paleozoic time. The eclogite-bearing subduction complex appears to be similar to the Triassic Dabie-Sulu UHP terrane in terms of occurrence, rock types, and P-T conditions, except for the Caledonian time of continental subduction and collision. The North Qaidam Mountains evidently constitute another coherent UHP metamorphic terrane, marking the NE tectonic boundary of the Tibetan Plateau the Caledonian suture zone between continental blocks in NW China.

V32C-0980 1330h POSTER

Relationship between UHP eclogite and two different types of granite in the North Qaidam, NW China: Evidence from zircon SHRIMP ages of granites

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The southern margin of the Qilianshan is a long, narrow mountain range extending from the Altyn Mtn southeastward to the Alciotoshan for about 800 km and