

that is easily released during weathering, thus black shales could potentially drive the observed variation in oceanic $^{187}\text{Os}/^{188}\text{Os}$ during the Cenozoic, a conclusion that has implications for the global carbon cycle and global climate change.

V31C-09 1055h

Stable Isotope Stratification of Neoproterozoic Seawater in a Post-Snowball Earth: Evidence From Deepwater Rocks of Western Canada

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As inferred from the $\delta^{13}\text{C}$ composition of marine precipitates, Neoproterozoic seawater has undergone dramatic changes in isotope composition driven by variable rates of organic carbon versus carbonate carbon burial. Much of the Neoproterozoic is characterized by ^{13}C -enriched values suggesting large proportional burial of organic carbon. Dramatic excursions to negative $\delta^{13}\text{C}$ values are associated with major glacial events. Diagenetic effects aside, a central problem to the interpretation of negative $\delta^{13}\text{C}$ isotope signals has been the degree of chemical stratification in seawater, a predictable consequence of large fractional burial of carbon as organic matter. The Windermere Supergroup (WSG) in western Canada comprises the depositional record of a passive continental margin that developed coeval with supercontinent (Rodinia) breakup and global glacial ("Snowball Earth") events. A unique feature of the WSG is the prevalence of deepwater sedimentary rocks, which record the history of element sequestration in the reduced reservoir that complements the existing global geochemical database, derived largely from shallow water oxidized facies. Analysis of $\delta^{13}\text{C}$ of organic and carbonate carbon pairs from regionally persistent stratigraphic units in the WSG demonstrates the robust character of the carbonate $d^{13}\text{C}$ signatures and suggest that carbonate compositions were largely rock-buffered during post-depositional diagenesis and low-grade metamorphism. Occurrences of shallow water carbonates, resedimented into the deep water during falls in sea level, carry with them the isotope record of shallow marine conditions from which they precipitated, which are persistently 5 permil enriched in ^{13}C relative to the deep water background values. Such an inferred gradient, is consistent with stratification of the isotopic composition of the seawater carbon pool driven by oxidation of organic matter in the water column and bacterial sulfate reduction. The latter process is confirmed by the presence of strongly ^{34}S -depleted sulfides in deep-water shales. Mixing of the ^{13}C -depleted deep water with ^{13}C -enriched shallow water in post-glacial times provides an alternative to the current Snowball model that suggest such negative excursions are the results of mantle buffering of the global carbon cycle during Snowball events.

V31C-10 1110h

Unraveling the Chronology of the Late Pleistocene Wilson Creek Formation, Mono Lake, CA

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An important challenge for understanding the dynamics of Earth's past climate system is to establish consistent time scales. It is increasingly important to find clear time lines for tying disparate high-resolution records together because the interpretation of relative time (leads and lags) among records is a major basis for modeling and interpreting driving mechanisms of climate change. Mono Lake is located adjacent to the eastern edge of the Sierra Nevada, and its extended

Pleistocene counterpart has been named Lake Russell. The Wilson Creek Formation, Mono Lake, CA, is the lacustrine deposits of the last glaciation. During glacial times when Sierra Nevada glaciers extended to their maximum glacial positions, and the lake was greatly elevated, icebergs floated in Lake Russell and deposited dropstones in the Wilson Creek Formation. We would like to understand the global context of these and other climatically driven variations in the Wilson Creek Formation. New C-14 results on residual carbonates after sequential dissolution indicate that modern carbon contamination effects are significant below 30 ka, and reduce the age in excess of 10 ky at the base of the formation.

The Wilson Creek Formation also contains 19 ash layers, 18 of which are rhyolitic eruptions from the Mono Craters, and they have been numbered from youngest to oldest (Lajoie, 1968 UC Berkeley Ph.D. thesis). Outcrops on the southeastern shores of Mono Lake have relatively thick and coarse deposits, and we have separated >0.8 mm sanidine crystals from ash layers #8, 15, and 16. Chen et al. (1996, Science) have previously reported Ar-Ar data from multiple individual sanidine crystals from ashes #5 and 12. The Ar-Ar results are also complicated. Analytical uncertainties of individual sanidine crystals are generally 1-5 ky, but the range of measured ages in some cases is greater than 50 ky. Accordingly, it is necessary to measure larger numbers of individual crystals and to take the youngest age population as the maximum age of the ash layer. For ashes #5, 12, 15, and 16 these are 23.1, 35.4, 49.9, and 51.4 ka respectively. A particularly sobering example is ash #8. Stratigraphically constrained to be 27 ka, 13 sanidines provide an isochron age of 763 ± 0.5 ka. These sanidines were probably derived from eruption through the nearby Bishop Tuff.

An outstanding feature of the Wilson Creek Formation that has great potential as a global time line is the Mono Lake geomagnetic excursion. In light of new C-14 and Ar-Ar results, and based on comparison of the Wilson Creek geomagnetic record with NAPIS-75 (Laj et al. 2000 EPSL) we suggest that the feature identified as the Mono Lake excursion at Wilson Creek is the Laschamp Geomagnetic Excursion with an age of 35 C-14 ky B.P. or 40 ka. The base of the Wilson Creek Formation is constrained to be greater than 50 ka, and may as old as 75 ka (MIS 5/4 boundary). Although uncertainties remain large, we are systematically working toward a precise and accurate age model for the Wilson Creek Formation.

V31C-11 1125h

Environmental Applications of $^{240}\text{Pu}/^{239}\text{Pu}$ Measurements Using the IsoProbe MC-ICP-MS

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The ability to determine the isotopic ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in low-Pu samples provides a powerful tool in environmental studies. Applications include the characterisation of the source of nuclear contamination and as a post-1950 dating tool.

Until recently alpha spectroscopy was commonly applied for measurements in environmental studies to determine plutonium activity concentrations. Owing to overlapping peaks it is unable to resolve of ^{240}Pu and ^{239}Pu and results are reported as of $^{239+240}\text{Pu}$. Some studies have used thermal ionisation mass spectrometry (TIMS) to determine of $^{240}\text{Pu}/^{239}\text{Pu}$ but preparation is difficult and the precision is poor. MC-ICP-MS (Micromass IsoProbe) offers an attractive alternative method since it provides better reproducibility, higher ionisation efficiency (0.2%) and requires less chemical separation. A precision of better than 1% is achieved for a Pu sample size of 0.5 pg (equivalent to 1.5mBq).

We present three novel applications demonstrating the usefulness of high resolution of $^{240}\text{Pu}/^{239}\text{Pu}$ measurements:

1. A UK salt marsh that has received Pu contamination since the early 1950s. shows that of $^{240}\text{Pu}/^{239}\text{Pu}$ can be helpful in understanding processes of sediment mixing and transport.

2. Studies of of $^{240}\text{Pu}/^{239}\text{Pu}$ in soil in the southern UK allow estimates of the relative contribution of Pu from weapons fallout and from aerosols discharged from a nuclear weapon factory.

3. Ice core samples taken from an Alpine glacier are investigated to determine a chronology for of $^{240}\text{Pu}/^{239}\text{Pu}$ in the atmosphere over Europe.

URL: <http://www.soc.soton.ac.uk/isotope>

V32A MC: Hall D Wednesday 1330h

Nanoparticles in the Environment II (joint with A, H, OS, P, MR)

Presiding: A Navrotsky, Univ of California-Davis; J Banfield, UC Berkeley

V32A-0953 1330h POSTER

Molecular-Scale Structural Controls on Nanoscale Growth Processes: Step-Specific Regulation of Biominerall Morphology

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Deciphering the complex strategies by which organisms produce nanocrystalline materials with exquisite morphologies is central to understanding biomineralizing systems. One control on the morphology of biogenic nanoparticles is the specific interactions of their surfaces with the organic functional groups provided by the organism and the various inorganic species present in the ambient environment. It is now possible to directly probe the microscopic structural controls on crystal morphology by making quantitative measurements of the dynamic processes occurring at the mineral-water interface. These observations can provide crucial information concerning the actual mechanisms of growth that is otherwise unobtainable through macroscopic techniques.

Here we use in situ molecular-scale observations of step dynamics and growth hillock morphology to directly resolve roles of principal impurities in regulating calcite surface morphologies. We show that the interactions of certain inorganic as well as organic impurities with the calcite surface are dependent upon the molecular-scale structures of step-edges. These interactions can assume a primary role in directing crystal morphology.

In calcite growth experiments containing magnesium, we show that growth hillock structures become modified owing to the preferential inhibition of step motion along directions approximately parallel to the [010]. Compositional analyses have shown that Mg incorporates at different levels into the two types of nonequivalent steps, which meet at the hillock corner parallel to [010]. A simple calculation of the strain caused by this difference indicates that we should expect a significant retardation at this corner, in agreement with the observed development of [010] steps. If the low-energy step-risers produced by these [010] steps is perpendicular to the c-axis as seems likely from crystallographic considerations, this effect provides a plausible mechanism for the elongated calcite crystal habits found in natural environments that contain magnesium. In a separate study, step-specific interactions are also found between chiral aspartate molecules and the calcite surface. The L and D- aspartate enantiomers exhibit structure preferences for the different types of step-risers on the calcite surface. These site-specific interactions result in the transfer of asymmetry from the organic molecule to the crystal surface through the formation of chiral growth hillocks and surface morphologies. These studies yield direct experimental insight into the molecular-scale structural controls on nanocrystal morphology in biomineralizing systems.

V32A-0954 1330h POSTER

Reactive Site Control during Dissolution of Biotite and Muscovite

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Despite several solution and mineralogical studies have been done on mica weathering, the way and fate by which this dissolution occurs is subject of controversy. Field and laboratory studies that estimate dissolution rates rely on measurements of exposed mineral surface area (geometric area), but the evolution of the

mineral surface area that really participate to the reaction remains, still, the most difficult parameter to characterize. In this study, the reactive surface area of biotite and muscovite has been qualitatively assessed in experiments performed in the fluid cell of an Atomic Force Microscope (AFM) at room temperature under high flow rate and pH values of 1.1, 3.3 and 5.7. Additional assessment was provided by the chemical composition of the output fluids. The molecular periodicity resolution of our AFM images shows that (001) pristine surface of micas before interaction consists on basal oxygen groups with hexagonal-like arrangement interpreted to correspond to the mica tetrahedral sheet. We have observed that dissolution produces etch pits with stair-step pattern, the height of first step corresponding to the sum of tetrahedral and octahedral layers (i.e.: 0.43nm (biotite), 0.45nm (muscovite)). During dissolution, pits growth producing new lateral (hk0) and basal (001) faces. In both micas, we found that the average velocity of step movement at the lateral face is 2-3 orders of magnitude higher than at the basal face and that only dissolution velocity of the lateral (hk0) face decreases as a function of solution pH. In addition, kinetic dissolution rate calculated by elements assured to be on octahedral layers (i.e.: Fe, Mg (biotite), Al (muscovite)) decrease as a function of pH, while, rate estimated by element on tetrahedral layer (i.e.: Si, Al (biotite and muscovite)) does not change significantly as a function of H⁺ ion activity. Since steps generates new lateral faces corresponding to the sum of octahedral and tetrahedral layers and, movement of the lateral face is faster than basal, we propose that the sites that are significantly active to the mica dissolution reaction correspond to that responsible for destruction of the octahedral layer.

V32A-0955 1330h POSTER

Molecular Models of the Structure and Hydration of Sodalite and Laumontite Zeolites

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An energy forcefield for the simulation of hydrated aluminosilicate zeolites has been developed to examine the structure and dynamics of water in nanoporous materials. Radial distribution functions for O-O, Na-O, and Ca-O in solvated ion systems, as well as unit cell volumes for hydrated sodalite (Na₆Al₆Si₆O₂₄H₂O), fully dehydrated sodalite, hydrated laumontite (Ca₄Al₈Si₁₆O₄₈H₂O), and partially dehydrated laumontite (12 and 14 H₂O/unit cell) have been used to validate and apply this forcefield. Molecular dynamics simulations (NVT canonical ensembles) were run for the water-cation systems, each comprised of 216 water molecules, a single cation, and with a density of ~1 g/cm³ at 300 K. The theoretical RDFs for the first hydration spheres of O-O, Na-O, Ca-O are 2.78 +/- 0.02 Å, 2.36 +/- 0.02 Å, and 2.48 +/- 0.02 Å, respectively. These results compare favorably to average observed values of 2.90 Å (-4.1%), 2.43 Å (-2.9%), and 2.42 Å (+1.8%), respectively. Energy minimization and molecular dynamics simulations for the various hydration states of sodalite suggest complex interactions between the water molecules and the zeolitic framework. In particular, water oxygens prefer to coordinate with the extra-framework cations, while the water hydrogens associate with other water molecules, and to a lesser extent, framework oxygens. Energy minimizations (at constant pressure) provide unit cell volumes of 732.0 Å³ and 759.7 Å³ for the two sodalite end-member structures, and these values compare well to average observed values of 693.4 Å³ (+5.6%) and 756.9 Å³ (+0.4%), respectively. Note the smaller unit cell volume for the fully hydrated structure, obtained from both simulation and experimental techniques. Theoretical hydration curves for sodalite, incorporating intermediate water contents, support the observed trend in unit cell volumes. A similar approach has also been used to examine the natural hydration states of laumontite, to evaluate the mechanisms of hydration, and to help interpret experimental hydration curves. In contrast to sodalite, energy minimization models of laumontite illustrate a more direct relationship between unit cell volume and water content. The unit cell volumes for partially and fully hydrated laumontite are 1402.8 Å³, 1424.9 Å³, and 1425.1 Å³, comparing well to average observed values of 1341.0 Å³ (+4.6%), 1366.0 Å³ (+4.3%), and 1380.6 Å³ (+3.2%), respectively. Finally, we use plane-wave pseudopotential density functional calculations to validate our potential-based simulation models. In the case of fully dehydrated sodalite,

our DFT simulations suggest that the sodium ions occupy the centers of the six-membered rings, in agreement with our forcefield results. This configuration is in contrast to the results of a recent DFT study, which suggests that the sodium ions are significantly offset from the planes of the six-membered rings.

V32A-0956 1330h POSTER

Phase Transformations in the GIS Structure upon Ion Exchange

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Important details of the dynamics of ion exchange are available only from time-resolved diffraction studies. In order to introduce contrast between T-sites in aluminosilicate ion exchangers we synthesized AlGe-analogues of the gismondine-related phases, Na-(Na₂₄Al₂₄Ge₂₄O₉₆*40H₂O) and K-AlGe-GIS (K₈Al₈Ge₈O₃₂*8H₂O) materials, which crystallize in space groups C2/c (a=14.490(3) Å, b=9.940(2) Å, c=23.530(5) Å, β=105.90(1)°), and I2/a (a=10.311(2) Å, b=9.749(1) Å, c=10.225(6) Å, β=90.000(2)°), respectively. These unit cells (I2/a cell to C2/c cell) are related by the transformation a = a; c = b; b = -a; c = -c with a shift in origin of (1/4a + 1/2c). Noting the appearance and disappearance of ordering (C2/c) reflections, indicating the presence of the larger ordered cell for Na-GIS, were used to monitor the exchange process. At approximately 50% exchange the C2/c cell transforms to the smaller I2/a cell, with a disordered arrangement of cations in the channels. Le Bail extraction was performed to accurately determine the unit cell parameters. Single crystal diffraction experiments were also done to check the cell parameters and unit cell contents.

V32A-0957 1330h POSTER

Thermodynamic Properties of Hydrotalcites

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Interest in hydrotalcite-like compounds has grown due to their role in controlling the mobility of aqueous metals in the environment as well as their use as catalysts, catalyst precursors and specialty chemicals. Although these materials have been studied in a number of contexts, little is known of their thermodynamic properties. Here we present a first-order model to estimate the enthalpy and free energy of hydrotalcite-like compounds by considering them as mechanical mixtures of simpler binary compounds. Specifically we have calculated a set of room temperature enthalpies and free energies of formation for cobalt-aluminum hydroxycarbonates by considering them as mechanical mixtures of several binary hydroxides and carbonates and nitrates. High-temperature oxide melt calorimetry was then used to measure the standard-state enthalpy of formation for the compounds Co_{0.68}Al_{0.32}(OH)₂(CO₃)_{0.16}

- 0.779H₂O (ΔH_{f,298}⁰ = -1044.17 ± 2.58 kJ/mol) and Co_{0.756}Al_{0.244}(OH)₂(CO₃)_{0.1202}(NO₃)_{0.0036}
- 0.710H₂O (ΔH_{f,298}⁰ = -967.90 ± 5.98 kJ/mol). Their enthalpy of formation from the binaries are 0.16CoCO₃+0.52Co(OH)₂+0.32Al(OH)₃+0.779H₂O → Co_{0.68}Al_{0.32}(OH)₂(CO₃)_{0.16}
- 0.779H₂O (ΔH_{f,298}⁰ = -5.06 ± 2.86 kJ/mol)
- 0.1202CoCO₃+0.634Co(OH)₂+0.0018Co(NO₃)₂+0.244Al(OH)₃+0.710H₂O
- Co_{0.756}Al_{0.244}(OH)₂(CO₃)_{0.1202}(NO₃)_{0.0036}
- 0.710H₂O (ΔH_{f,298}⁰ = -12.56 ± 6.17 kJ/mol)

Since the enthalpy of formation of these compound from the end members is near zero the calorimetric data support the model. It might then be applied to other transition metal systems to estimate their standard-state thermodynamic properties.

V32A-0958 1330h POSTER

Energetics of Nanocrystalline TiO₂

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This study focuses on the determination of enthalpy of subsequent derivation of surface enthalpies (J/m²) of these polymorphs. Nano-crystalline anatase, brookite, rutile, mixtures of anatase and rutile, and mixtures of anatase and brookite are studied using high temperature molten oxide drop solution calorimetry. The calorimetric results are corrected for water and for impurities, if any. Since the energetics of these TiO₂ polymorphs are closely balanced, the particle morphology, strain, and chemical synthesis conditions influence the presence of a particular phase. We have studied nanorutile samples with surface area of 1758 - 5833 m²/mol (22 - 73 m²/g). A plot of enthalpy of nanorutile samples versus surface area yields the surface enthalpy of rutile as 2.2 ± 0.2 J/m². A nanoanatase sample (~12000 m²/mol) and a nanobrookite sample (~6400 m²/mol) have enthalpies of 7.02 ± 0.96 kJ/mol and 7.11 ± 1.13 kJ/mol, respectively, higher than bulk rutile. Efforts to separate surface energies and transformation enthalpies (for bulk anatase-rutile and brookite-rutile) from the energetics of these nanocrystalline samples are in progress.

V32A-0959 1330h POSTER

Study of Hydrothermal Particulate Matter from a Shallow Venting System, offshore Nayarit, Mexico

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A shallow (30 ft) hydrothermal site named "Cora" (after the indigenous people thereby) was surveyed and sampled throughout direct observation with SCUBA diving during November 25 to December 4, 2000. A total of 10 dives were conducted in order to obtain representative samples from an 85°C fluid source of approximately 10 cm in diameter. Inherent difficulties to

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) Archimedeian 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.

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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.

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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