Title
Calculations of montmorillonite structure using density functional theory

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The simulations show the effects of a three-dimensional surface topography on elastic wave propagation. Ground motion at the surface is severely affected by topography. If neglected, this may jeopardize attempts to determine source location by analyzing particle motion. Numerical studies like this can help to understand wave propagation phenomena observed on field recordings in volcano seismology. Future studies will aim at separating the wave effects of internal scattering, topography and sources (tremors, tectonic events, pyroclastic flows).

V31B MC: 305 Wednesday 0830h

Nanoparticles in the Environment I

(joint with A, H, OS, P, MR)

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

V31B-01 0830h

Characterization of Colloidal Nanoparticles Released from Hg-bearing Mine Wastes

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The release of mercury from mine waste tailings at historic mining sites in the California coastal ranges is a significant pollution threat to local water sources and fish populations. The transport of mercury associated with nanometer-scale (50-400 nm) colloidal particles is one of the major pathways for mercury release from these mine sites. This study has used laboratory column ex-periments to generate colloids from calcines and unprocessed waste rock from the New Idria (NI) and Sulphur Bank (SB) mines. Colloid generation was initiated by flowing two solutions of vary-ing ionic strength through the columns in the presence of malonic acid. The colloidal material generated was characterized by ATEM, Extend X-ray absorption fine structure (EXAFS) analysis, and chemical sequential extraction techniques.

ATEM analysis indicates that the colloids generated from the NI calcines consist of crystalline alunite-jarosite and hematite, a poorly ordered Si-Al gel and HgS. This mixture is very similar to that present in the bulk calcine material and suggests that these colloids are formed by detach-ment/breakup of the bulk material. Hg-LIII-EXAFS and sequential extractions indicate that 90% of the mercury present in these colloids is in the HgS form. The column experiments on the SB calcines produced only a small amount of colloidal material when the first few pore volumes of solution were flowed through. These consist of quartz, poorly ordered Si-Al-Fe gel and HgS. Hg-LIII-EXAFS spectra confirms that HgS is the dominant mercury species in these colloids. Raising the pH of the colloid-free column effluent from the SB calcines experiment results in the precipita-tion of a poorly ordered Si-Al-Fe rich gel, which is similar to that observed at the waste pile/lake interface next to the SB mine (Clear lake, CA). EXAFS and ATEM results indicate that mercury can be associated with this precipitated colloidal material. Colloids generated using unprocessed waste rock from the SB mine site consist of Cr-oxide, hematite, mackinawite (FeS0.9), and HgS formed via the detachment/breakup mechanism. As for the two previous systems Hg-EXAFS re-sults indicates that HgS is the dominant mercury-bearing phase in these colloids.

This study shows that the colloidal transport of mercury from these particular mine sites occurs predominantly as HgS and not as Hg sorbed to minerals phase as previously thought. Also the mechanisms of colloid generation (i.e. detachment/breakup or dissolution/reprecipitation) varies according to the composition of the starting material.

V31B-02 0845h

Grain Boundary Carbon in Synthetic Quartzite: Implications for Electrical Conduction in the Crust

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Despite the repeated implication that grain boundary graphite forms electrically connected networks in the earth's deep crust, little is known about the equilibrium microstructure of graphite at high pressures and temperatures. To evaluate this, we conducted several piston cylinder experiments designed to equilibrate carbon with crystalline SiO_2. In one set of experiments, stacked single crystal (SC) disks of polished quartz were coated with 0 to 150 nm of carbon film in 50 nm increments. The stacks were positioned horizontally in graphite capsules and were heated at 1.4 GPa to 1150°C for 48 hours in one experiment, and to 1500°C for 0.05 and 5 hours in two others. In another set of experiments, we produced two polycrystalline (PC) quartzites in textural equilibrium with small amounts of carbon. A powder consisting of 75-150 μm grains of natural crystals was fired for three days at atmospheric P and 1000°C and coated with a 30-50 nm carbon film. In one experiment, the powder was encased in a graphite capsule; in the other, a Pt capsule was used. Both were equilibrated for 120 hours at 1300°C, 1 GPa.

Polished sections of the products revealed that the low-T SC run contained a thin, dark film on all interfaces including the uncoated face; the short duration, high-T SC run contained a dark film on all of the coated interfaces, but not on the uncoated interface; and the longer duration, high-T SC run contained isolated opaque blebs that increased in density with increasing thickness of the initial film. Additionally, these SC products contained a small number of fractures with thin, dark films, blebs, or dendrites. Both PC experiments produced similar products, largely composed of polygonal quartz grains and apparently unconnected small dark grains located along grain boundaries. Most of these dark grains exhibited a rounded or globular morphology, but a few showed rational faces.

The results suggest that carbon films are not stable along quartz grain boundaries. Instead, carbon appears as rounded shapes that are likely to be interconnected only at elevated volume fractions. However, the presence of films in the lower T and short duration experiments may point to relatively sluggish kinetics for carbon textural equilibrium, and therefore to the possibility that carbon films may be present as transient features in the crust.

URL: http://www.rpi.edu/~pricej/work/C/

V31B-03 0900h

Adsorption of Water on the TiO_2 (Rutile) [110] Surface: A DFT Study

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Periodic DFT calculations (CASTEP) using slabs separated by vacuum gaps were carried out to model the H_2O-TiO_2 (rutile) [110] interface. Positions of all atoms were allowed to relax except atoms in the central layer of the slab. Both associative (i.e., Ti-OH_2) and dissociative (i.e., 2 TiOH) adsorption mechanisms were considered for 1/2 monolayer and monolayer coverages. Five different orientations of H_2O molecules on the TiO_2 surface were studied to determine the most energetically favorable water positions. Two slab thicknesses (3 Ti layers and 5 Ti layers) were chosen to test the effect of slab depth on calculated surface structures. Results indicate that associative adsorption is favorable by 8 to 15 kJ/mole/H_2O depending on the slab thickness for full monolayer coverage, whereas the opposite was calculated for 1/2 monolayer coverage. The associative adsorption mechanism is consistent with experiment. The role of H-bond formation on the adsorption energies and structures will be discussed.

V31B-04 0915h INVITED

Surface Charge and Ion Sorption Properties of Titanium Dioxide

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The interaction of submicron metal oxide particles with natural aqueous solutions results in the hydroxylation of surface sites, which impart a pH-dependent surface charge. The charged submicron particles influence processes such as nanoparticle assembly and alteration, crystal growth rates and morphologies, colloid flocculation, and contaminant transport.

The surface charge and ion sorption properties of metal-oxide particles may be studied by potentiometric titrations, using hydrogen-electrode concentration-cells or traditional glass electrodes and an autotitrator. These techniques have been used to quantify the adsorption of various ions (Na^+, Rb^+, Ca^{2+}, Sr^{2+}, Cl^-) on rutile, at ionic strengths up to 1.0 molality and temperatures to 250°C. The crystalline rutile used in these studies is less than 400 nm in diameter, has a BET surface area of 17 m^2/g, and the 110 and 100 faces predominate. The negative surface charge of the rutile was enhanced by increasing temperature, increasing ionic strength, and decreasing the ionic radii of the electrolyte cation. Moreover, the addition of a divalent cation significantly enhances the negative charge of the rutile surface. These data have been rationalized with the MUSIC model of Hiemestra and van Riemsdijk, and a Basic Stern layer description of the electric double layer (EDL). Model fitting of the experimental data provides binding constants for the adsorbed counterions and divalent cations, and capacitance values as well as corresponding electrical potential values of the binding planes.

Recently, new studies have been initiated to determine particle size affects on the proton induced surface charge and ion sorption properties of titanium dioxide. In these studies, anatase with a BET surface area of 40 and 100 m^2/g (primary particle sizes of 40 and 10 nm, respectively) is being investigated. The complexity of both the experimental and modeling procedures increases with decreasing particle size. For example, the fine-grained powders must be adequately dispersed, and agglomeration must be minimized during titration. Moreover, when rationalizing the experimental data, curvature of the nanoparticles must be accounted for in the description of the EDL. Preliminary experiments suggest that the proton induced surface charge of 10nm anatase is similar to that of rutile at 25°C in 0.03m RbCl media.

V31B-05 0930h INVITED

Nanoscale Structure at Mineral-Fluid Interfaces

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The nature of nanoparticles and their role in the natural environment is currently a subject of renewed interest. The high surface area (and surface area-to-volume ratio) of nanoparticles exerts a widespread influence on geochemical reactions and transport processes. A thorough understanding of the nanoscale world remains largely hypothetical, however, because of

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the challenges associated with characterizing nanoscale structures and processes. Recent insights gained from high-resolution synchrotron x-ray reflectivity measurements at the solid-fluid interfaces of macroscopic (i.e., mm-scale) mineral particles may provide relevant guidelines for expected nanoparticle surface structures. For example, at calcite-water and barite-water interfaces, undercoordinated surface cations bond with water species of variable protonation, and modest relaxations (to several hundredths of a nanometer) affect the outermost unit cells [1,2]. Undercoordinated tetrahedral ions at aluminosilicate surfaces also bond with water species, whereas interstitial or interlayer alkali or alkaline earth ions at the surface may readily exchange with hydronium or other ions; modest relaxations also affect the outermost unit cells [3,4]. Modulation of liquid water structure out to about one nanometer has been observed at the (001) cleavage surface of muscovite in deionized water, and may be present at other mineral-fluid interfaces [4]. Dissolution mechanisms at the orthoclase-water interface have been clarified by combining x-ray reflectivity and scanning force microscopy measurements [5]. Further progress in understanding nanoscale structures and processes at macroscopic mineral-water interfaces is likely to benefit nanoparticle studies.

[1] Fenter et al. (2000) Geochim. Cosmochim. Acta 64, 1221-1228. [2] Fenter et al. (2001) J. Phys. Chem. B 105(34), 8112-8119. [3] Fenter et al. (2000) Geochim. Cosmochim. Acta 64, 3663-3673. [4] Cheng et al. (2001) Phys. Rev. Lett., (in press). [5] Teng et al. (2001) Geochim. Cosmochim. Acta 65, (in press).

V31B-06 1005h

Calculations of Montmorillonite Structure Using Density Functional Theory

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Montmorillonite is a 2:1 clay mineral that is ubiquitous in terrestrial weathering environments of temperate zones. Its high surface reactivity with cations and organic molecules make it one of the most important natural nanoparticles determining the geochemical cycles of metals and carbon in soils, water bodies, and the atmosphere. Mechanistic understanding of its surface reactivity depends on accurate molecular-scale information. Recent advances in powerful first-principles methodologies, such as density functional theory, and in the computational implementation of these methodologies, have made it possible to perform realistic simulations of nanoparticle structure and reactivity. We have begun simulations of this kind, emphasizing clay minerals in the smectite group, notably montmorillonite. Total-energy calculations with ultrasoft pseudopotentials and plane-wave basis functions were performed on montmorillonites of varying layer charge using density functional theory with energy optimization. All calculations were performed with Cray T-3E and IBM SP RS/6000 supercomputers at the National Energy Research Scientific Computing Center (NERSC). Full atomic coordinates with the unit cell geometry of montmorillonite were determined quantum mechanically for the first time. Important structural features, including surface corrugation, tetrahedral rotation, interatomic distances, and interatomic angles were compared with theoretical and/or experimental values for montmorillonite and for pyrophyllite, which is structurally isomorphic to montmorillonite but without layer charge. The effect of charge substitution and interlayer cation on the structure, especially its hydroxyl groups, was studied systematically. Simulated X-ray diffraction patterns and IR/Raman spectra also were obtained for montmorillonite and pyrophyllite. These quantum mechanical calculations of clay mineral structure, which require no adjustable parameters, gave excellent results for both equilibrium structures and total energies.

URL: http://esd.lbl.gov/GEO/aqueous_geochem

V31B-07 1020h

Kinetics of Crystal Growth in Synthesis of Silicalite-1

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Previous studies have shown that (a) silicalite-1 or pure silica MFI zeolite containing tetrapropylammonium (TPA) ions can be synthesized from an apparently clear solution - 9.00TPAOH-25.0SiO2-480H2O-100.0EtOH; (b) pre-assembled primary particles (PPs) of about 3 nm diameter possessing the structural and compositional features of the large TPA-MFI crystals are already formed in the initial solution; and (c) upon heating, the nucleation and crystal growth proceed by an addition mechanism of the PPs. Our in situ calorimetric investigation reveal that the crystal growth at 95 C is associated with a first exothermic event and followed an endothermic event. The abrupt thermal switch coincides with a sharp rise in pH (12.6 to 13.3). The change from exothermic to endothermic is rather intriguing because it implies a strong entropy driving force, which may arise from the release of small molecular species (like H2O and/or OH-) from the eliminating interface to the liquid phase. During the exothermic period, the crystal yield is linearly proportional to the integral enthalpy. The size of the crystal increases linearly with crystallization time. The pH of the synthesis solution remains unchanged (12.6). Thus the rate of the linear crystal growth during the exothermic period can be directly derived from the calorimetric curve. In this study, in situ calorimetric syntheses at various temperatures (75 100 C) are examined. The activation energy for crystal growth is derived based on the calorimetric data. The results and their implication for zeolite synthesis mechanisms are further discussed.

V31B-08 1035h

In situ, Time Resolved Small Angle Solution Scattering: A Synchrotron-Based Study of the First Minute in the Life of Iron Sulphide and Iron Oxihydroxide Colloids

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Environmental remediation programs rely on the understanding of the formation mechanisms and kinetic rates of iron sulphide and oxyhydroxide colloids because they control the mobility and bioavailability of toxic compounds in contaminated aqueous systems. Such iron-based colloids form ubiquitously as ultra-fine particles suspended in the anoxic or oxic water, or as coatings on mineral grains and their high specific areas and very reactive surfaces regulate the removal of toxic trace elements (e.g., As, Cd, Cr) from a contaminant plume. However, the formation mechanisms and the kinetic growth rates for such reactive iron colloids are not well established and the rates at which such colloids remove toxic metals from solutions is poorly understood. The dearth of data on the mechanism controlling the first steps in the nucleation and growth of Fe-S and FeOOH phases from an aqueous solution is mainly a consequence of the fact that the nucleation reactions are extremely fast and, in both systems, strongly pH, redox and temperature dependent. Here we present data from synchrotron-based, *in situ*, small angle X-ray scattering (SAXS) experiments that were carried out with the goal to characterize the first stages (20 milliseconds to 60 seconds) in the nucleation and growth of ferrous sulphides and hydrated ferric oxides in aqueous solutions. The experiments were carried out using a stopped flow system equipped with a quartz sample capillary, 3 reservoir syringes and 2 mixers with a dead volume of 10 μL and a dead time of 10 milliseconds. This set up warranted fast and precise mixing of two solutions with the capability for data acquisition at speeds of 20 to 500 millisecond per scan. From the obtained scattering data, information on rates of nucleation, changes in size and shape of the colloids during growth, as well as the growth kinetics and fractal dimension of FeS and FeOOH phases during their precipitation from solution could be derived.

V31B-09 1050h INVITED

Unlocking Metal Sequestration in Soils Nanoparticles

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Control of the mobility of toxic elements in natural systems and waste depositories, and the remediation of contaminated soils, sediments, or subsurface waters, are major goals of environmental geochemistry. These goals cannot be met without first having in hand a fundamental understanding of the elemental composition, spatial distribution, and chemical form of trace elements in environmental nanoparticles. Key problems in understanding how elements interact with environmental constituents at the molecular level are the partitioning of elements into coexisting minerals, the difficulty of identifying the mineral species to which these elements are bound, and the multiplicity of sorption mechanisms. Hard x-ray microscopy, one of the important new probes emerging from the current generation of synchrotron sources, offers unprecedented opportunities for molecular environmental science. In most cases, the information sought can be obtained by a synergistic use of synchrotron-based X-ray microfluorescence (micro-SRXF), microdiffraction (micro-XRD), and microspectroscopy, including micro-XANES and micro-EXAFS. X-ray microanalysis (micro-SRXF) is for mapping the distribution of trace contaminants among coexisting mineral phases in a natural matrix, thus determining their concentrations with unrivaled sensitivity. Microdiffraction allows the identification of nanoscale minerals. micro-XANES gives the oxidation state of sorbed elements, and micro-EXAFS opens the way for determining the uptake mechanism of trace contaminants by individual mineral phases. Since trace element sorption is heterogeneous on nanometer to micrometer length scales, the combination of these chemical and structural techniques provides just the tool needed to scrutinize fundamental properties. These new scientific opportunities will be illustrated by the sequestration mechanism of Zn and Ni in soils. It will be shown with this example how laterally resolved synchrotron microtechniques can be used to make the key identification of important metal constituents and their speciation in the environment.

V31B-10 1105h

Condensed Volcanic Aerosols Collected Near-Source at Poas

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Volcanic plumes are mixtures of gases and liquids that react with air to form aerosols. In this study, atmospheric samples were collected near fumarolic vents at Poas Volcano inside the crater and 380m away on the crater rim. Aerosols were captured on supportive Cu grids coated by a thin C-film, encased within a sealed collector designed for this experiment. Grids were exposed to plume constituents for 30-seconds then frozen to prevent further reaction before analysis. Morphologic and chemical features were examined by TEM, Energy Dispersive X-Ray Spectroscopy (EDS) and Atomic Force Microscopy (AFM).

A thin heterogeneous coating of Si and lesser Fe with minor, variable Cl and S covers the C-film. Solid particles additionally contain O and Mg. Liquid droplets of splattered appearance containing Na, Mg and O, lesser amounts of K, Ca and Cl, and minor S and Fe, are surrounded by satellite droplets and radially symmetrical dendritic patterns. Varied components in single droplets suggest that near source, liquids are not necessarily differentiated. O found in particles and droplets but not in the coating may demonstrate partitioning of O out of the condensable gaseous phase. These two observations show that differentiation has begun, but is not completed, at short distances from source.

Liquid droplets of varying heights (15-35nm) and diameters (300-500nm) are topped with smaller (5nm high; 50nm diameter) domes. A mottled surface covers morphological highs and flat areas. Contraction marks that grew wider as analysis progressed extend between and linearly across the surface of the droplets. Different size droplets could represent fluids of differing surface tensions growing to individually preferential size,

or droplets that have not achieved ideal size. Smaller domes atop larger ones may be gases escaping.

These samples represent a portion of volcanic plumes that must be studied to understand the evolution of volcanic aerosols, and, consequently, their influence on atmospheric chemistry. We observe that components begin partitioning immediately upon interaction with air. This observation combined with the tendency of some gases to form a liquid phase supports the idea that measurements made kilometers away from source may be underestimates.

V31B-11 1120h INVITED

Deciphering the Physical Basis of Biomineralization through Investigations of Nanoscale Growth Processes

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Microbes and higher organisms direct the formation of complex structures in controlled biomineralization. Using biologically mediated crystallization strategies that have evolved over millenia, organisms have developed the ability to produce nanophase structures as single crystals and composite materials with remarkable properties that fulfill specific functional needs. Modern organisms, as well as those found in the sediment and rock records, chronicle Natures ability to synthesize sophisticated nanostructures. Although biomineral compositions and their morphologies are windows to interpreting environments of prosperity and decline, most current interpretations lack an understanding of fundamental processes. Hence, the physical basis of biological mineralization continues as one of Natures best kept secrets.

Recently, the biomineralization processes of marine microorganisms have emerged as particularly important owing to the use of biomineral products as paleoclimate indicators. Besides providing critical information on crystal growth history, the minor and trace elements found in these materials also behave as impurities to regulate their properties and formation rates. Using integrated approaches, we are investigating the kinetics and thermodynamics of calcite growth to decipher mechanisms of biomineral formation. Our focus is to link molecular interactions with surface processes and nanoscale controls on crystal morphology. The molecular-scale structure of the crystalline interface is a critical growth determinant, especially when considering nanocrystalline phases.

By combining in situ AFM studies of growth that use carefully characterized solution chemistries with molecular modeling and surface spectroscopic investigations, we couple observations of nanoscale growth mechanisms with quantitative kinetic and thermodynamic information. This approach is showing how key inorganic growth impurities, Mg2+ and Sr2+, affect mineralization through complex ion-specific mechanisms. We also show how simple amino acids affect growth by modifying the energetics of step edges to produce unusual structures that reflect the chirality of bioactive compounds. These findings indicate that complex mineral formation may be best deciphered by understanding nanoscale controls on the direction-specific kinetics of step flow and the intertwined controls of surface thermodynamics.

V31B-12 1135h

Characterization of the Biogenic Mn-Oxide Produced by *Pseudomonas putida* Strain MnB1

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Mn-oxide nanoparticles are common and highly reactive materials in the environment. They occur as dispersed colloids, in nodules, and as coatings having high specific surface areas and, thus, high surface reactivity. Hence, they are believed to play a major role in the fate and transport of contaminant and nutrient species in the environment. Most of these oxides are believed to be microbial in origin, and a wide array of Mn(II) oxidizing bacteria exists in almost all natural aqueous environments. However, little is known about the structures, characteristics and reactivities of these biogenic oxides. The goal of this research was to identify the Mn oxide product from a strain of the fresh water bacterial species *Pseudomonas putida*, and to characterize it along with analogous synthetic Mn oxides: two different Mn^{III}/Mn^{IV} oxides identified as birnessites, and the Mn^{IV} oxide, δ-MnO_2. These synthetic phases were defined as potential models based on comparison to X-ray absorption and diffraction spectra from a large number of Mn(II/III/IV) references. Characterization of biotic and abiotic Mn oxides was performed with respect to: morphology, surface area, Mn composition, structure, and surface reactivity. In this fashion, randomly-stacked hexagonal birnessite of low crystallinity was identified as a close synthetic analog to the biogenic oxide, making it suitable for reference and comparison purposes, as well as for reactivity prediction studies. This synthetic product is distinct from monoclinic birnessite, but showed some similarities to Mn oxide minerals of very low crystallinity previously identified as vernadite (δ-MnO_2). This latter mineral has been identified in the past as comparable to the biogenic oxide produced by the marine *Bacillus* sp. strain SG-1, which suggests similarities in the biological Mn(II) oxidation processes across natural environments and bacterial species.

V31C MC: 304 Wednesday 0830h

Geochemical and Isotopic Tracers of Earth Processes: Low Temperature Geochemistry and Paleoclimate (a session in honor of Gil Hanson) *(joint with H, T, GC, MR)*

Presiding: **S R Hemming,** Lamont-Doherty**; J Hurowitz,** SUNY Stony Brook

V31C-01 0835h

Boron Isotope Compositions of Sediment Interstitial Brines, ODP Leg 182, Great Australian Bight

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ODP Leg 182 drilled a cool-water biogenic carbonate platform in order to gain information regarding higher latitude climate proxies, tectonic/eustatic sea-level effects, as well as the biological regime of these settings. An unexpected observation was the presence of a brine with salinity up to 3 times normal seawater. We have analyzed boron isotopes and boron concentrations in pore water samples from sites 1127 and 1130 to help constrain the source of the high salinities.

B isotopes were measured on an Axiom multi-collector ICP source mass spectrometer. Mass 11 and 10 were measured in static mode, and the inherent large fractionation resulting from the ICP source was corrected by bracketing each sample run with a standard. Although boron was extracted from samples using ion exchange columns, a residual matrix effect remains with this procedure. This was minimized by using seawater treated identically to samples as the normalizing standard during the mass spectrometer analyses. Reproducibility of this method is better than +/- 0.5 per mil, 2 sigma.

It has been postulated that the high salinity is due to evaporative concentration of seawater during subaerial exposure of the shelf, and subsequent flow of these brines into the carbonate sediment. However, the boron data indicate that in both sites 1127 and 1130 this cannot be the only process involved, and the significant differences in the trends of the two cores indicate that the processes may be different at the two sites. The boron isotopic compositions of the interstitial waters from both cores are significantly offset from seawater by as much as -17 per mil. This light composition is consistent with several processes, including dissolution of carbonates or desorption of light B from marine clays. However, clays are not a significant in these sediments. The low pH of the interstitial waters is consistent with the carbonate dissolution scenario. The concentration of B shows a positive covariation with Sr concentration while the B isotope compositions tend to be negatively correlated with B and Sr concentrations. These trends are all consistent with carbonate dissolution as being the primary mechanism responsible for the variation in the B isotopic composition. However, the expected correlation between B isotope composition and Ca concentration is not consistent with this process. A possible explanation for this discrepancy is recrystallization of high Mg calcite and aragonite as low Mg calcite which takes less B and Sr than the precursor minerals.

High Na/Cl values observed in these porewaters (higher than normal seawater) are associated with evidence for the presence of gas hydrates, possibly due to uptake of Cl by the hydrates. The Na/Cl is elevated in both cores, but site 1127 has a distinct peak in the Na/Cl at a core depth of about 100m (Na/Cl peaks at a value of 1.04), while site 1130 shows a rise in the Na/Cl above seawater values down to about 50m, and then remains constant down core at about 0.85. Little is known about the effects of gas hydrates on the boron system, but a correlation between B concentration and Cl concentration may hint at a hydrate influence. Further study of these cores including high resolution B isotope analyses may further constrain the possible mechanisms that are controlling the water compositions.

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Meteoric Water Influx, Gypsum and Halite Dissolution, and Fluid Mixing on the Flanks of the South Liberty Salt Dome, Texas Gulf Coast.

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Brine samples were collected from non-geopressured oil-bearing horizons of the Frio, Yegua and Cook Mountain Formations along the flanks of the South Liberty Dome, Liberty County, Texas. The dome is capped with gypsum, anhydrite and minor calcite. Twenty six water samples were analyzed for Na, K, Ca, Mg, Si, Al, HCO_3, CO_3, Cl, SO_4, Br, I, P, Li, B, Ba, Mn, acetate, δD and $\delta^{18}O$. Data from several 2-D seismic lines were used for interpretation of sequence stratigraphy and structure of the sediments in the area.

The water is a Na-Cl brine with dissolved solids ranging from 68,000 to 208,000 mg/L. The fluid source as indicated by chemical and isotopic tracers is brine from the surrounding geopressured sediments mixing with the local meteoric water. This brine shows a mixing trend, with increased meteoric water fraction with decreased depth. This mixing trend occurs across formations and in some areas it appears to follow a migration pathway. All of the samples, excepting one, show evidence of halite dissolution with elevated Na and Cl concentrations; nine of these samples also show evidence of gypsum dissolution, with SO_4 up to 2,000 mg/L. Samples with the greatest gypsum dissolution are located very near the dome and show the greatest fraction of meteoric water, suggesting that meteoric water influx to depth is the greatest at the margins of the salt/host rock contact. [The Texas Higher Education Coordinating Board Advanced Research Program supported this research.]

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A 12,000-Year Record of Climate of Central Taiwan

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There exists now overwhelming evidence that the climate of the last 12,000 years has undergone more than one cycle of global warming and cooling. The results of ice cores from Greenland and Antartica and of deep sea cores from North Atlantic and other areas also reveal that the transition between the two states of climate is very rapid. Previously, we reported our finding of similarly rapid transition during Younger Dryas event in Central Taiwan. Evidence of this short-term cycle and rapid transition, however, is generally lacking from tropics and subtropics. This is a progress report on our investigation into the climate records of Taiwan.

Samples from the upper 8 meters of a 39-meter long peat bog core of a late Quaternary fresh water lake at Toushe, Central Taiwan, were analyzed for their carbon-isotope composition to study their climate records. The ^{14}C-age at 8 meter depth of the core is about 12350 years BP. The present altitude of the sampling site is about 650 meters and it is at 23°49'N and 120°53'E.

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