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.

V31C-02 0850h

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 δ^{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.]

V31C-03 0905h

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.

The results reveal a climate record similar in general to, but different in specific from many of North Atlantic deep-sea and Greenland ones. For example, they clearly show Bölling-Allerod warm/humid followed by Younger Dryas cold/dry period and short-term climate fluctuation during Holocene; and the results also show three "very warm" episodes centering at the middle of the Bölling-Allerod warm period, at the end of demise of Younger Dryas cold period at about 5000 year BP, repsectively. There are at least six relatively warm and six relatively cold periods during Holocene. The time span between any two consecutive warm and cold periods is not perfectly but roughly equal. In other words, the period of short-term climate cycle is, on the average about 1500 years.

In conclusion, the climate records od central Taiwan and the above mentioned climate records od Greenland, Antartica and North Atlantic are similar in general features but different in details and maybe in timing of events.

V31C-04 0920h

Geochemistry of Aerosols in North -West India

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The geochemistry of, sources to, and transport of dust and their consequences on earth system processes are least understood. Here we follow Guru Gil's approach to use trace elements and isotopic data on aerosols in northwest India to understand their sources and processes. Aerosol samples were collected over a stretch of 550 kms from the Thar desert to the Delhi region which sits on the eastern fringe of the Thar. This region witnesses frequent dust storms in summer seasons due to high intensity south westerly and westerly winds. Major, trace elements including REE and Sr isotopic data are generated on three different group of aerosols such as dry deposition (DD, >100μm), suspended particulate matter (SPM, 0.1-100μm) and PM10 (<10μm) collected by different sampling techniques and at different seasons.

Major and trace elements in all DD samples show a high degree of homogeneity with similar LREE enriched patterns and -ve Eu anomalies regardless of space and time of sampling. These particles are geochemically similar to UCC, PAAS, and local loess with relatively low CIA values, indicating a low degree of chemical weathering suffered by their source regions dominated by upper crustal materials. Geochemistry of SPM and PM10 aerosols shows variation along the wind path. With decreasing size, crustal component decreases, anthropogenic inputs to transition metals and non-silicate input to Ca budget increase. The greater variability in finer fractions is primarily due to anthropogenic input and local meteorology where wind acts as an intensive variable. The REE patterns in SPM and PM10 are similar to DD samples with -ve Eu anomaly but their abundance decrease with size, probably due to some dilution effect by organics and mineralogical factors. It is possible that REE hosting minerals are concentrated in coarser silt and finest sand fractions (35-70μm). This is supported by the decreasing Zr concentrations with decreasing size and distance in downwind direction where the wind velocity reduces. ^{87}Sr/^{86}Sr isotopic ratios of all the fractions also show a small size dependency. The coarser samples have higher values (0.719-0.720) compared to finer ones (0.715-0.717). These values are similar to the lower end of Indo-Gangetic alluvium ratios (J. Tripathy), perhaps resulting from the minor addition of Jurassic carbonate/gypsum, present in the upwind part.

Thus, the source for the dominant component of aerosols is upper crustal and is likely to be older Himalayan alluvium deposited by now defunct rivers in the Rajasthan region. The removal of silty materials (a dominant part of aerosols) from the older alluvium is probably responsible for the presence of Thar desert in the upwind direction.

V31C-05 0935h

Application of Geochronology and Geochemistry of Speleothems to Hydrologic Change

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Carbonate cements deposited from groundwater in caves (speleothems) over recent geologic time offer great potential for understanding processes of hydrologic and environmental change. Geochemical and isotopic variations in speleothems have been used as records of continental paleoclimatic and hydrologic variables. Studies of multiple speleothem samples from carbonate aquifer systems in central Texas and Barbados provide insight into the mechanisms and timescales that link climatic and hydrologic processes. A critical constraint in understanding such links is time. Speleothems can provide terrestrial climate proxies with continuous temporal and spatial sequences of growth. They are precisely datable over a range of timescales for the Pleistocene and Holocene using the U-Th and U-Pa geochronometers. Speleothems that grew over the last 70,000 years in three caves in the Edwards aquifer of Texas yield concordant ages by these two methods. These results are consistent with the closed-system behavior of these geologic materials and indicate the potential for constructing accurate time series. High-resolution speleothem growth rate variations are a new tool for assessing variations in regional hydrologic and climatic change.

A hydrologic model that explains changes in groundwater flow routes in karst aquifers as a function of rainfall-recharge can account for many of the geochemical trends both observed in modern groundwaters and recorded in speleothems. Controls on fluctuations in Sr isotopes, and trace elements include 1) varying fluxes of dissolved constituents from geochemically distinct sources (i.e., soils versus host limestones), 2) residence time, and 3) water-rock interaction pathways. Within an aquifer system, trace element - isotope co-variations illustrate the influence of local soil compositions on the geochemical evolution of both modern groundwater and Pleistocene speleothem calcite. An approach integrating geochemical and isotopic techniques suggests that in spite of the many complexities of regional and local variability both within and between aquifer systems, climate signals are discernable. Coupled studies of speleothems and the modern groundwater system help constrain mechanisms that link hydrologic and climatic processes over multiple timescales. The calibration of modern speleothem geochemistry and growth rates with aquifer and climatic measurements is a new research avenue toward this end.

V31C-06 0950h

U- and Th-Series Transport in a Sandy Aquifer in an Arid Climate

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We investigated the transport of U-Th series nuclides of an aquifer in an arid region with low flow velocities, the Ojo Alamo Aquifer of the San Juan Basin, which has ^{14}C water ages up to 25 kyr (Phillips et al. 1989; Stute et al. 1995). The study aims to test a theoretical transport model by Tricca et al. (2000) with data from an aquifer with lower groundwater flow velocities (4×10^{-6} cms^{-1} compared to 10^{-4} cms^{-1}). U, Th, Ra and Rn activities and major ion abundances were analysed. Compared to the previous study, groundwaters have high U concentrations ($C_U \sim 20 - 200$ ppt) and very high δ^{234}U values from 5,000 to 11,000. The C_U of spring and river waters are much higher (0.7 to 12 ppb). The δ^{234}U values range from 500 to 700, far lower than the groundwaters. The present vadose and river water thus are completely distinctive from the aquifer water, and cannot be a significant source to the aquifer (<< 10%). Estimating the groundwater age using the flow distance, an average weathering rate of U within the aquifer is calculated. These estimated rates vary between 10^{-18} to 10^{-16} s^{-1}. The model predicts that δ^{234}U values depend upon the fraction of recoil ^{234}Th ejected from the rock compared to the weathering rate. The high δ^{234}U values can easily be produced with low recoil fractions of 10^{-4} to 10^{-2}. Applying the same model to a vadose zone thickness of 20 meters, with water infiltration rates of half the rainfall (22 cm/yr) and soil moisture contents around 10%, it is found that weathering rates and the recoil fraction are much higher in the vadose zone. Very high C_U in the springs are caused by low infiltration rates through a vadose zone with low moisture content, and rapid weathering of smaller mineral grains in the soils. Lower C_U in the groundwater indicate a disconnection between the spring waters and the rest of the groundwater, or that the high C_U measured from the springs are contaminated (from an unknown source). Filtered C_{Th} are less than 0.3 ppt. The C_{Th} appears to be controlled by local solubility limits, so that Th is precipitated on surfaces within the aquifer. The activities of Ra isotopes are similar to values from a sandy aquifers from a temperate region (Tricca et al. 2000). Measured ^{226}Ra activities are much less than parent U activities and do not correlate. ^{228}Ra/^{226}Ra activity ratios are between 1.5 and 4, the supply ratio from the host sediments, and are dominated by a source in secular equilibrium. The Ra is dominantly adsorbed onto surfaces in exchange equilibrium with the local groundwater. Activities of ^{222}Rn gas are similar to those found in other localities (50 to 450 dpm/kg). These values require emanation factions of up to 10% if the host rock is the direct source. However, the irreversible precipitation of ^{230}Th and ^{232}Th within the aquifer may provide a source for the ^{222}Rn which does not require special recoil processes specific to Rn. In accordance to the model, we conclude that high C_U in the vadose zone can be generated by high recoil and weathering rates in arid regions. The aquifer is distinct from the vadose zone with lower recoil fraction and weathering rates, although the apparent hydrologic disconnect between the two zones remains problematic.

We acknowledge the invaluable help from the Navajo Tribal Utility Authority.

V31C-07 1025h INVITED

Rock Varnish: Recorder of Desert Wetness?

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Rock varnish is a thin coating (<200 μm) of a cocktail rich in Mn, Fe, and clay minerals that is ubiquitous in desert regions. It has become the center of a contentious controversy revolving around its use to date geomorphic surfaces and/or to evaluate past climate conditions. We observe pronounced temporal variations in Mn and Ba concentration that are similar over large regions and that likely relate to variations in paleo-wetness. The mode of formation of varnish remains uncertain, but anthropogenic Pb concentrated in outermost varnish layers indicates its continued formation, and experiments using cosmogenic Be suggest that, while precipitation is a primary control, dust, dew, and aerosols may also be important in delivering the ingredients of varnish. We suggest several steps that may lead to rejuvenation and future breakthrough in varnish studies.

V31C-08 1040h

Constraints on Sources of Osmium to the World's Oceans: Combined 186Os/188Os and 187Os/188Os Evidence.

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The Os isotopic composition of marine Mn nodules provides a record of Cenozoic seawater evolution, and places constraints on sources of Os to the ocean. Used together, the 187Re-187Os and 190Pt-186Os systems provide complementary information that can distinguish between potential sources of Os to seawater. Marine Mn nodules that we have analyzed have radiogenic and variable 187Os/188Os, from 0.85 to 1.03. By contrast, measured 186Os/188Os for most of these nodules are chondritic. Five analyses of separate powders from a single nodule give a precise average 186Os/188Os of 0.119829 $\pm$ 11 (2 σ pop.), in close agreement with the chondritic value of 0.119834. Thus, although the average source of Os to the oceans is enriched in 187Os, the 186Os/188Os is not resolvable from chondritic values.

Estimates of the Pt/Os of average upper crust have suggested that it has a suprachondritic 186Os/188Os. We have analyzed two samples of loess from Long Island, NY, that have suprachondritic 186Os/188Os values of 0.119863 $\pm$ 16 (2 σ mean) and 0.119845 $\pm$ 10, and 187Os/188Os of 0.75 and 0.67, respectively. In addition, a fresh-water Mn concretion from Lake Oneida, NY provides an estimate of the average isotopic composition of Os that is released into the hydrosphere. This concretion also has a supra-chondritic 186Os/188Os of 0.119852 $\pm$ 7 (187Os/188Os = 1.92).

The observation that the increase in seawater 187Os/188Os over the last 15 Ma is mirrored by a decrease in its δ13C has prompted suggestions that an increase in weathering rates of sufficiently aged black shales could account for the trend. We have analyzed four Paleozoic black shales; all have very high 187Os/188Os (from 7.8 to 11.6) and 186Os/188Os that are essentially chondritic. These compositions suit the requirements for a source of Os to the modern oceans that can produce variable and radiogenic 187Os/188Os, but maintain a chondritic 186Os/188Os. Black shales also have abundant Os (orders of magnitude higher than average upper continental crust)

that is easily released during weathering, thus black shales could potentially drive the observed variation in oceanic 187Os/188Os 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 δ^{13}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 δ^{13}C values are associated with major glacial events. Diagenetic effects aside, a central problem to the interpretation of negative δ^{13}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 δ^{13}C of organic and carbonate carbon pairs from regionally persistent stratigraphic units in the WSG demonstrates the robust character of the carbonate d13C 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 Earths 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}Pu/^{239}Pu Measurements Using the IsoProbe MC-ICP-MS

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The ability to determine the isotopic ratio of ^{240}Pu/^{239}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 $^{239+240}$Pu. Some studies have used thermal ionisation mass spectrometry (TIMS) to determine of ^{240}Pu/^{239}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}Pu/^{239}Pu measurements:

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

2. Studies of of ^{240}Pu/^{239}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}Pu/^{239}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 Biomineral 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