

hydrogen outgassing rate from interior of the Earth is not necessary to maintain high hydrogen concentration in Archean atmosphere. Since it is easier to maintain high methane concentration in a high hydrogen concentration atmosphere, the new solution of hydrodynamic escape supports methane rich atmosphere in the Archean era.

#### PP21B-1173 0830h POSTER

##### Glacial-Interglacial Atmospheric CO<sub>2</sub> Change –The Glacial Burial Hypothesis

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Organic carbon buried under the great ice sheets of the Northern Hemisphere is suggested to be the missing link in the atmospheric CO<sub>2</sub> change over the glacial-interglacial cycles. At glaciation, the advancement of continental ice sheets buries vegetation and soil carbon accumulated during warmer periods. At deglaciation, this buried carbon is released back into the atmosphere. In a simulation over two glacial-interglacial cycles using a synchronously coupled atmosphere-land-ocean carbon model forced by reconstructed climate change, I found a 547 Gt terrestrial carbon release from glacial maximum to interglacial, resulting in a 60 Gt (about 30 ppmv) increase in the atmospheric CO<sub>2</sub>, with the remainder absorbed by the ocean in a scenario in which ocean acts as a passive buffer. This is in contrast to previous estimates of a land uptake at deglaciation. This carbon source originates from glacial burial, continental shelf and other land areas in response to changes in ice cover, sea level, and climate. The input of light isotope enriched terrestrial carbon causes atmospheric  $\delta^{13}\text{C}$  to drop by about 0.3‰/‰ at deglaciation, followed by rapid rise towards a high interglacial value in response to oceanic warming and regrowth on land. Together with other ocean based mechanisms such as change in ocean temperature, the glacial burial hypothesis may offer a full explanation of the observed 80-100 ppmv atmospheric CO<sub>2</sub> change.

#### PP21B-1174 0830h POSTER

##### An Ice-Free Siberia: A Clue to Carboniferous CO<sub>2</sub> Levels

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Heretofore paleo-CO<sub>2</sub> levels have been estimated by geochemical models or proxies (stomatal indices, fossil soil composition). A complementary approach to this problem is that of inverse modeling. In brief, for the period in question oxygen isotopic evidence is used to infer a given amount of continental ice volume, and one or more climate models with dynamic ice sheet components are run to determine which CO<sub>2</sub> level is compatible with the predicted ice volume. While this method holds considerable promise, uncertainties in certain model inputs (paleolatitude, topography, salinity) may result in a very wide range of hindcast CO<sub>2</sub> levels. However, for the late Carboniferous a constraint may be imposed on the ensemble of model runs. There is no compelling evidence for significant Siberian glaciation in the Carboniferous, although Siberia is posited to be at a relatively high paleo-latitude and isolated from other continents – an ideal configuration for the establishment of permanent ice. Thus by reducing our ensemble of model runs to those in which the Siberian ice sheet is nonexistent we can constrain the modeled paleo-CO<sub>2</sub> predictions. Preliminary energy balance/ice sheet model (EB/ISM) results indicate that the effectiveness of this constraint will itself depend to a degree on the paleo-topography. At present the constraint on CO<sub>2</sub> value seems stronger for our 320 Ma simulations than for 360 or 280 Ma. For this interval our “best guess” CO<sub>2</sub> level for little/no Siberian ice is 3X present levels – somewhat higher than the 1X estimates from stomatal data and the Berner geochemical model.

#### PP21B-1175 0830h POSTER

##### Isotopic and Climate Model Constraints on Paleo-CO<sub>2</sub> in the Late Paleozoic

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Atmospheric CO<sub>2</sub> is one of the most important drivers controlling ancient climate and one of the hardest to quantify. We have combined three methods for quantifying paleoclimate, a coupled energy balance-ice sheet model (EB/ISM), an atmospheric general circulation model (AGCM), and oxygen isotope analyses of fossils, to constrain late Paleozoic pCO<sub>2</sub> levels. Our estimated pCO<sub>2</sub> is that which yields the same ice volume determined using two independent approaches, a  $\delta^{18}\text{O}$ -AGCM method and an EB/ISM. We calculate ice volume from the  $\delta^{18}\text{O}$  of brachiopod shells and AGCM temperatures ( $\delta^{18}\text{O}$ -AGCM method). Brachiopod shell  $\delta^{18}\text{O}$  values depend on two variables, ambient temperature and seawater  $\delta^{18}\text{O}$ . Using the oxygen isotope paleotemperature equation and ambient temperatures derived from AGCM results, we calculate seawater  $\delta^{18}\text{O}$ . From this seawater  $\delta^{18}\text{O}$  we use  $^{18}\text{O}$  mass balance to calculate ice volume. We run the AGCM with various values of pCO<sub>2</sub>, which produce different temperatures and different  $\delta^{18}\text{O}$ -derived ice volumes. Ice volumes deduced from brachiopod  $\delta^{18}\text{O}$  increase with pCO<sub>2</sub>. Ice volumes as a function of pCO<sub>2</sub> are also determined from the ice sheet model in the EB/ISM, and those ice volumes decrease with increasing pCO<sub>2</sub>. Our estimated pCO<sub>2</sub> is the intersection of the two ice volume-pCO<sub>2</sub> curves. Three different time slices and paleogeographies have been investigated in detail: 360, 320, and 280 Ma. GENESIS 2 AGCM simulations were performed at 1x and 4x modern preindustrial levels (280 ppm) for all time slices, and at 8x pCO<sub>2</sub> for 360 Ma. EB/ISM simulations were run with and without topography, with lapse rates of 5 and 7 °C/km, and with outgoing infrared radiation (OIR) ranging from 187.3 to 205.3 W/m<sup>2</sup>, equivalent to pCO<sub>2</sub> levels of 1x to 16x. EB/ISM simulations yielded ice volumes ranging from 0 to greater than 129 x 10<sup>6</sup> km<sup>3</sup>, depending on lapse rate, topography, and outgoing IR radiation. The highest ice volumes were obtained with topography, 7 °C/km lapse rate, and high OIR. The 320 Ma paleogeography generated the largest ice volume for a given input set. Interestingly, this is approximately the timing of initiation of major Carboniferous glaciation. Combining brachiopod  $\delta^{18}\text{O}$  values for North America and the Russian Platform with AGCM temperatures yielded ice volumes of 18 to 89 x 10<sup>6</sup> km<sup>3</sup> for 320 and 280 Ma, depending on pCO<sub>2</sub>. Isotopic results for 360 Ma, a time generally considered to be ice-free, produced negative ice volumes. Using topography and a realistic lapse rate of 5 °C/km, the EB/ISM and oxygen isotope models for 320 and 280 Ma generated similar ice sheet volumes at 2x to 3x pCO<sub>2</sub>. These values are similar to or slightly higher than results from geochemical models and pCO<sub>2</sub> proxies. Work is ongoing to explore variation in brachiopod  $\delta^{18}\text{O}$  values, and to investigate ice sheet volumes generated at different lapse rates and from uncoupled AGCM/ice sheet simulations.

#### PP21C MCC: Level 2 Tuesday 0830h

##### Pre-Quaternary Climate: Models and Observations Posters (joint with A, OS, C, GC)

Presiding: M Lyle, Boise State University

#### PP21C-1176 0830h POSTER

##### Geoclimate: The Study of Earth's Deep-Time Climate

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Earth's climate system operates on a continuum of temporal, spatial, and parametric scales. Climate variability on all these scales has, during Earth history, been much greater than is captured in the Quaternary record, especially given the recent changes in atmospheric composition that have pushed atmospheric CO<sub>2</sub> to pre-Miocene values. To address the current and future states of climate research on Earth's pre-Quaternary record, NSF recently sponsored a workshop attended by both geoscientists who model paleoclimate, and those who collect and analyze paleoclimate data. Several major science themes and issues require attention in order to achieve a holistic understanding of Earth's climate system, such as the (1) nature of the CO<sub>2</sub>-climate link, and evolution of atmospheric composition, (2) long-term record of the ecosystem-climate relationship, (3) interaction of climate components at various time scales, (4) prediction of thresholds, and drivers of different rates of change, (5) tectonic-climatic and climatic-eustatic interactions, (6) solar and orbital controls on climate change, and (7) coupling of multiple components, (ice sheets, vegetation, aerosols) in climate models. Research in paleoclimate model development and multi-proxy development, aided by greater collaboration between those who model paleoclimate and those who reconstruct paleoclimate, will catalyze progress in the study of earth's deep-time climate record. Based on the workshop discussions, there is a clear need for community input to further articulate research issues in both computation-based paleoclimate modeling and data-based paleoclimate reconstruction. To view the full workshop report, and provide such community feedback on possible future directions in deep-time paleoclimatology, please visit <<http://geoclimate.ou.edu>>.

URL: <http://geoclimate.ou.edu>

#### PP21C-1177 0830h POSTER

##### Thorium/U systematics of Precambrian deep-sea pelagic black shales: implications for redox state of the early atmosphere

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To address the question of the redox state of the Precambrian atmosphere-hydrosphere system via sediments requires measurement of redox sensitive trace elements, and inter-element ratios, in deep water black shales with a chemical sedimentary “hydrogenic” component. This approach is endorsed by recent progress in research of redox-sensitive trace metals records in late Proterozoic and Phanerozoic sedimentary rocks, which has provided important clues to how the redox state of depositional environments has changed over time. Many conventional studies, in contrast, have been on first cycle volcanogenic turbidites with a minimal hydrogenic input (Taylor and McLennan, 1995). Accordingly, we have analyzed the redox-sensitive, trace element compositions of the 2.1 Ga black shales in Birimian Blet, West Africa, and the 2.7 Ga Archean counterparts in Timmins, Canada, Tati Belt, Botswana, and

Kanowna District, Western Australia. These pyrite-bearing black shales, which were originally argillaceous sediments containing organic matter and low in thermal maturity, were primarily deposited in the deep-sea pelagic environments. Th/U ratios are lower in the Proterozoic shales (0.38-0.82, average 0.67), and Archean shales (0.47-3.65, average 2.43) relative to "conventional" Archean upper crust (3.8), PAAS (4.7), or average upper continental crust (3.8). Calculated U concentrations from hydrogenic component are between 0.90 and 2.45 in the Proterozoic shales, and range from 0.06 to 0.96 for the Archean black shales. Given the conservative behavior of Th in the sedimentary cycle, variably low Th/U ratios in these Precambrian black shales signify that  $U^{6+}$ , soluble in oxidized surface waters, was reduced to insoluble  $U^{4+}$  in reducing bottom waters, as in the contemporary Black Sea. The results are consistent with a locally to globally oxidized atmosphere-shallow hydrosphere pre-2.0 Ga. Taylor, S.R., and McLennan, S.C., 1995. The geochemical evolution of the continental crust: Reviews of Geophysics, v. 33, p. 241-265.

#### PP21C-1178 0830h POSTER

##### Experimental Constraints on Hydrothermal Fe-flux in Archean-Like Sea Water: Implications for Fe Transport in the Precambrian Seas and Precipitation of Banded Iron Formation.

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Determining the source of Fe for Banded Iron Formation (BIF) and reconstructing conditions that lead to their deposition is crucial to our understanding of the early evolution of the geochemical and biogeochemical processes that have come to dominate the modern Earth. The majority of BIF was precipitated between 2.8 and 1.7 Ga during a time of anoxia and low sulfate conditions in seawater. Fe-rich plumes of hydrothermal origin are thought to be the main source of Fe for BIF formation during this time, though estimates of Fe-flux needed to form these deposits suggest higher hydrothermal heat fluxes and/or fluid-rock reaction temperatures greater than indicated by modern vent systems. pH and dissolved Cl in hydrothermal systems, however, have been shown to greatly influence Fe solubility. Estimates from Archean fluid inclusion data indicate that dissolved Cl and Ca may have been higher than modern seawater by factors of approximately two and twenty, respectively. A relatively high dissolved Ca concentration could buffer pH during hydrothermal alteration at low values owing to constraints imposed by the solubility of Ca-bearing hydrous silicates. Thermodynamic data indicate that the effect of this is even greater at relatively low pressure - a condition that can be inferred from geophysical models for Archean hydrothermal systems. Thus, the combination of high Ca and Cl, with low hydrostatic pressure at the base of ancient MOR-related hydrothermal systems could have provided dissolved Fe fluxes in great excess of modern hydrothermal systems. We conducted a series of experiments to test the solubility of Fe in Archean-like seawater coexisting with basalt at high-temperature (350-400°C), low-pressure (300 bars) hydrothermal conditions. Based on estimates of Archean ocean composition (De Ronde et al., 1997), we prepared Archean-like artificial seawater composed of Na (789.0 mmol/kg), K (19.0), Mg (51), and Ca (232) with a total of 1374 mmol/kg Cl. Experiments were performed in a flexible gold reaction cell, which permitted sampling at elevated temperatures and pressures and monitoring of fluid chemistry with reaction progress. Fluid samples at 350°C indicated an average of 5.14 mmol/kg of Fe in solution, considerably higher than for modern systems at similar temperatures. When temperature was increased to 400°C, however, dissolved Fe increased by nearly an order of magnitude (40.1 mmol/kg). We interpret this dramatic increase in dissolved Fe to be chiefly the result of pH lowering induced by Ca-metasomatism associated with the formation of epidote and/or Ca-amphibole minerals after plagioclase. In effect, loss of Ca generates acidity, which is then balanced largely by an increase in Fe (Ca-Fe exchange). H<sub>2</sub>S concentrations revealed only a 2-fold increase to a maximum value of 12.0 mmol/kg, when temperature was increased from 350 to 400°C. The absence of dissolved sulfate in the starting fluid precludes additional H<sub>2</sub>S formation from sulfate reduction during basalt alteration. Thus, Archean vent fluids were likely characterized by high Fe/H<sub>2</sub>S ratios, which would greatly limit precipitation of Fe as sulfides near vents sources, enhancing delivery of Fe to the ancient ocean. Our results showing high Fe solubility combined with relatively low H<sub>2</sub>S concentrations confirm

that hydrothermal plumes can be an unusually effective source of Fe for BIF deposition during the middle Precambrian.

#### PP21C-1179 0830h POSTER

##### Snowball Earth Condition in AGCMs: Effect of Season and Continental Distribution.

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Using Atmospheric General Circulation Model (AGCM) coupled with a slab ocean (50m depth water), the snowball condition is investigated by searching the response of the earth to solar constant and CO<sub>2</sub> change systematically. The studies with and without season as well as that with and without continents are also compared. The system is under the partially ice covered condition (some ice on the earth and open ocean exists) for a broad range of external forcing, ex. 15 per cent of present solar constant and is consistent with other GCM studies. The response of AGCM to external forcing is quite different from that of EBM (energy balance models) in case the ice edge locates at mid to low latitude, preventing the system from falling into snowball condition. The reason for the persistent ice edge of AGCM compared to conventional EBM is partly due to the role of latent heat transport and also the seasonality.

#### PP21C-1180 0830h POSTER

##### Guadalupian-Lopingian (Middle-Upper Permian) boundary of mid-oceanic paleo-atoll limestone in Japan

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The Guadalupian-Lopingian (G-L) boundary sections of mid-oceanic origin were first examined in Japan by detail fusulinacean biostratigraphy. The Middle to Upper Permian reef-type limestone at Kamura and Akasaka in Southwest Japan occurs as allochthonous block in the Jurassic accretionary complex in Southwest Japan. These limestone blocks were derived from ancient mid-oceanic (paleo-Pacific or Panthalassa) atolls on seamount. The 36 m thick limestone section at Kamura and the 124 m thick one at Akasaka span across the G-L boundary as demonstrated by fusulinacean faunal change; both the Kamura and Akasaka sections are divided into 3 fossil zones, i.e., Lepidolina-Yabeina Interval Zone + barren interval of the Guadalupian (Middle Permian) and overlying Codonofusiella-Reichelina Interval Zone of the Wuchiapingian (Late Permian). The base of the Wuchiapingian is defined by the FAD of the *Codonofusiella* and *Reichelina* assemblage without any neoschwagerinids, verbeekinids, and schwagerinids. The results of this study suggest that extinction of large fusulinaceans such as neoschwagerinids, verbeekinids, and schwagerinids at the G-L boundary occurred also in mid-ocean in addition to continental shelf areas. Both at the two study sections, a sharp lithologic change is recognized at the G-L boundary; the Lepidolina-Yabeina Interval Zone and barren interval is composed of black limestone, while the overlying Codonofusiella-Reichelina Interval Zone of light gray dolomitic limestone. This lithologic change suggests a remarkable paleoenvironment change in mid-ocean around the G-L boundary. Besides the lithofacies change, a sharp decline of  $\delta^{13}C_{carb}$  values is detected just below the G-L boundary at the Kamura section. The sharp changes both in  $\delta^{13}C_{carb}$  values and in lithofacies across the G-L boundary support that the environmental change was global in extent, and this may have led the G-L boundary mass extinction.

#### PP21C-1181 0830h POSTER

##### The Environmental Impact of the Paleocene-Eocene Thermal Maximum on the Coastal Ocean, New Jersey: Inferences from Stable Isotope, Trace Metal, and Organic/Inorganic Carbon Records

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Approximately 55 million years ago, the Earth experienced an abrupt transient global warming, the Paleocene-Eocene Thermal Maximum (PETM). Two shallow marine sections across the PETM were cored near Clayton, New Jersey. Nannofossil biostratigraphy along with carbon isotope stratigraphy were used to identify the boundary and to constrain the thickness of the PETM. The excursion layer appears to be expanded (15 m), though the early Eocene is truncated by erosion. The Wilson Lake and Clayton cores, along with data from other northeastern U.S. localities within the same embayment, reveal significant biologic and mineralogical anomalies across the CIE. For example, the Wilson Lake core contains a pronounced increase in relative abundance of dinoflagellate cysts (dinocysts) assigned to the genus *Apectodinium* around the event, increasing from <1% below the CIE transition to 52% within, as well as a pronounced spike in kaolinite content. A suite of geochemical analyses including stable isotopes was generated for the Wilson Lake core at high resolution to constrain temperature/salinity, organic/inorganic C fluxes and redox conditions. The isotope records show dramatic negative excursions in  $\delta^{13}C$  and  $\delta^{18}O$ , with a 6‰/‰ negative carbon shift in bulk sediments. Carbonate content decreases to <1% at the  $\delta^{13}C$  bulk minimum and then increases to a maximum of 15% 3 m above. The benthic and planktonic foraminifer isotope records show excursions but of much smaller magnitudes than recorded in bulk carbonate implying a meteoric diagenetic overprint on the bulk isotope signal. Uranium, manganese, and barium data indicate minor shifts in the redox conditions of bottom waters during the excursion. Substantial manganese enrichment over much of the interval suggests that oxidative conditions dominate during the event consistent with the low organic carbon content (<1%). At the top of the section, a spike in uranium indicates a shift to suboxia in the late stages of system recovery. The lack of barium enrichment during the event suggests that there was little change in local paleoproductivity.

#### PP21C-1182 0830h POSTER

##### Ocean-Atmosphere Interactions in the Caribbean and Tropical East Pacific During the Early Pliocene

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Pliocene planktonic stable isotope records and Mg/Ca temperature reconstructions from ODP Sites 999, 1000 and 1241 were used to examine atmospheric and oceanic teleconnections between the Caribbean and tropical eastern Pacific. Our studies focus on the time interval from 5.5 to 3 Ma that is affected by an increase in Caribbean sea surface salinity (SSS) in response to the progressive closure of the Central American Seaway. The comparison of *G. sacculifer*  $\delta^{18}O$  records from Caribbean Sites 999 and 1000 indicates a strong increase in SSS towards the North with amplitude fluctuations of up to 3 units between 4.2 and 3.8 Ma. During this time interval, sea surface temperatures (SST) and SSS are positively correlated and reveal pronounced 23 kyr cycles. At tropical east Pacific Site 1241, variability in surface water hydrography is also dominated by precession and half-precession cycles. The strong response of SSS and SST to orbital precession suggests a low latitude climate forcing as the potential trigger. Precessional variations in the tropical wind field associated with small-scale latitudinal fluctuations of the Intertropical Convergence Zone (ITCZ) as well as changes in the hydrological cycle would explain the observed changes in SST and SSS. The long-term behavior of ENSO fluctuations may have contributed to the relatively large fluctuations in Caribbean SSS.

#### PP21C-1183 0830h POSTER

##### Millennial-Scale Variability of Western Equatorial Atlantic Ocean Thermocline Depth: Evidence From the Early Pliocene

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We use high-resolution oxygen isotope data from planktonic foraminifera in the Western Equatorial Atlantic (Ocean Drilling Program Leg 154, Site 925) to investigate millennial-scale climate variability during an interval of relative climate warmth, the early Pliocene. For this purpose, we have chosen a 100 kyr long time interval from 4.1 Ma to 4.2 Ma and sub-sampled it to obtain an average time step of 700 yr. We reconstruct changes in mixed layer depth using the difference in oxygen isotope values ( $\Delta\delta^{18}\text{O}$ ) between Globigerinoides sacculifer, a mixed-layer dweller, and Neoglobobulimina dutertrei, a thermocline dweller. Time series analysis of the  $\Delta\delta^{18}\text{O}$  records indicates that temporal changes in mixed layer depth occur at sub-Milankovitch periods of between 10-5 kyr. Similar variability during this interval of time has been observed in lacustrine sediments from the Mediterranean region (Steenbrink et al., 2003). Our results suggest that millennial-scale variability may be a pervasive climate signal during this interval of relative global warmth. As mixed layer depth in the western tropical Atlantic is a function of trade wind strength, we believe that millennial-scale variability in mixed layer depth during the early Pliocene is also tied to changes in wind patterns. We speculate that the millennial-scale changes in mixed layer depth at site 925 reflect millennial-scale variability in trade wind strength and direction perhaps linked to the interaction between low latitude insolation and the North African monsoon.

#### PP21C-1184 0830h POSTER

##### Middle Miocene Climate Change and Carbon Cycle: Milankovitch Forcing and Deep Ocean Circulation in the Western Pacific and Eastern Indian Ocean

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The relation of enhanced carbon burial, carbon isotope excursions and global cooling remains an unsolved problem in the Mesozoic and early Neogene climate history of the Earth. The enigmatic long-term positive carbon isotope excursion between 16.4 and 13.6 Ma ("Monterey excursion") coincided initially with a period of extreme warmth and high sea level (mid-Miocene climate optimum) and a subsequent increase in deep-water oxygen isotopic values, related to the cooling of deep water masses and growth of the East Antarctic ice sheet. High resolution reconstruction of the succession of events reveals a complex relationship between orbital forcing, carbon burial and climate cooling, mediated by a major re-organization of ocean circulation patterns. We used high resolution benthic deep water oxygen and carbon isotopes in combination with new age models at critical locations in a West Pacific marginal basin (South China Sea, ODP Site 1146), in the eastern Indian Ocean (NW Australian margin, ODP Site 761) and in the tropical Pacific (Ontong Java Plateau, ODP Site 806) to investigate the frequency and amplitude of deep water isotope fluctuations during the middle Miocene. Benthic stable isotope records document complete recovery of the six main  $\delta^{13}\text{C}$  maxima of the Monterey Excursion" between 16.4 and 13.6 Ma and the characteristic stepped increase in  $\delta^{18}\text{O}$  between 14.5 and 13.1 Ma. At Site 761, the  $\delta^{18}\text{O}$  curve shows an excellent match with the global sea level curve between 11.5 and 15.1 Ma, and thus closely reflects changes in global ice volume. Prior to 15.1 Ma, the  $\delta^{18}\text{O}$  curve is mainly driven by bottom water temperature. At Site 1146, a major increase in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values ( $1^\circ/\text{oo}$ ) at 14.0 Ma, indicates a radical change in the deep water circulation of this marginal West Pacific basin. Spectral analysis of benthic isotopes time series, combined with magnetic susceptibility and color reflectance records, indicate Milankovitch forcing on virtually all proxies and a change from eccentricity to precession driven cyclicity at approximately 14.8 Ma. The  $\delta^{13}\text{C}$  curve closely reflects the eccentricity forcing of Laskar's astronomical solution. Strikingly, a period of anomalous eccentricity forcing between approximately 14.8 and 14.1 Ma coincides with the fifth carbon maximum and initiation of major global cooling. Variations in the global carbon cycle modulated by eccentricity probably played a major role in controlling mid Miocene climate evolution.

#### PP21C-1185 0830h POSTER

##### North Pacific Sea Surface Temperature, Western U.S. Vegetation, and the Demise of the Miocene Rocky Mountain Monsoon

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Between 15 Ma and 5 Ma the vegetation of the western U.S. suffered a profound transition from summer-wet to summer-dry flora. In the middle Miocene extensive deciduous forests covered the region, reminiscent of modern forests of the SE United States. By the beginning of the Pliocene, however, these western monsoon forests disappeared and were replaced by vegetation adapted to a Mediterranean climate regime (summer-dry, winter-wet) or by desert vegetation. The change was largely gradual—the west began drying out by about 12 Ma. Extensive grasslands first appeared in eastern Oregon about 7-8 Ma, and the last of the exotic Miocene deciduous forest disappeared from the northern California coastal region by 5 Ma. The disappearance of summer precipitation in the west has traditionally been attributed to either the development of a rain shadow to the east of the mountains and/or cooling of the north Pacific Ocean. However, two important lines of evidence indicate that the development of a Sierra/Cascade rain shadow cannot have been the dominant process in the drying out of the western U.S. The gradual drying trend from at least 12 Ma to 5 Ma does not coincide with the known tectonic histories of either the Cascades or the Sierra Nevada range. More importantly, the disappearance of the Miocene flora on the coastal side of the mountain ranges cannot be attributed to a developing rain shadow. Instead the disappearance of coastal flora require a weakening of the moisture source from the north Pacific. We suggest that the drying of the west resulted from stepwise cooling of the north Pacific, which caused the gradual disappearance of a Miocene Rocky Mountain monsoon and a gradual but drastic reduction of summer precipitation. During the middle Miocene, summer sea surface temperatures were relatively warm off the West Coast, feeding moist air into the interior of the western U.S. During the late Miocene, a gradual cooling trend in the north Pacific related to reorganizations of Miocene Pacific circulation eventually cut off this summer supply of moist air. Prior to 8 Ma, diatom censuses indicate that Japan and the California margins had similar temperatures, indicating a relatively warm California current. Between 8 and 5 Ma, cooling of north Pacific waters occurred in a stepwise manner, resulting in enhanced coastal upwelling along the California coast, the appearance and expansion of sea-ice diatoms in the Bering Sea, and the first appearance of ice-rafted sediments in the northwest Pacific by 5.5 Ma. Understanding the dynamics and demise of the Rocky Mountain monsoon will be important for understanding how water and heat are transported into the interiors of continents during periods of extreme warmth. Rates of change of western U.S. water supply are intimately linked to the rate of change of north Pacific sea surface temperature.

#### PP21C-1186 0830h POSTER

##### Cenozoic Climate Evolution of Northeastern Tibet: Carbon and Oxygen Isotope Results From the Qaidam Basin, Western China

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Carbon and oxygen stable isotope analyses on carbonates from the nonmarine, endorheic Qaidam basin in Western China yield cycles of various length and order and show several distinct events related to regional climate and tectonism.

Situated at the northeastern margin of the Tibetan plateau and enclosed by three large mountain belts, the Altyn in the northwest, the Eastern Kunlun in the south and the Qilian mountains in the east, the Qaidam basin provides a unique research area. The basin has an up to 17, in average 8 kilometers-thick Cenozoic sedimentary sequence of lacustrine-terrestrial, partly hypersaline strata. Through most of its lifetime arid, hypersaline conditions were dominating, interrupted by semiarid periods resulting in a large lake during Miocene. Such changes can be observed in the stable isotope record. About sixty deep water carbonate and marl samples from Eocene to Holocene formations from the northwestern part of the Qaidam basin have been analyzed.

There is a general trend towards arid and highly evaporative conditions over Cenozoic time, visible in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  records. Carbon isotope data of the Hongsanhan section reveal two shorter cycles, which are interpreted as part of a higher-order cycle. This higher-order cycle shows a clear trend towards more arid conditions through time. The oxygen data stay in a narrow range between -8 and -6 $^\circ/\text{oo}$  until late Oligocene, then they start to vary more strongly.

Three distinct tectonic events can be detected: A distinct drop in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of 3 $^\circ/\text{oo}$  and 1 $^\circ/\text{oo}$ PDB, respectively at ca. 24 Ma reflects Himalayan uplift. At 19-18 Ma an excursion towards warm and dry conditions coincides with the phase of strongest uplift in the Altyn Mountains. A relatively humid interval appears around 12 Ma simultaneous with pronounced subsidence of the Qaidam basin. The increasing aridity and evaporative conditions in Quaternary are well reflected by the positive delta-values of both carbon and oxygen isotopes. A Quaternary sample yielded an extremely high value of +8.69 $^\circ/\text{oo}$   $\delta^{18}\text{O}$  for matrix material. This represents the most positive value ever measured in a sedimentary rock.

#### PP21C-1187 0830h POSTER

##### Covariation of $\delta^{44/40}\text{Ca}$ and pH in Ocean Surface Waters during the Neogene

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Neogene planktonic foraminifera were collected from cores of ODP Sites 871/872 in the western equatorial Pacific Ocean (*Globigerinoides trilobus*) and ODP Site 1138 in the Indian sector of the Southern Ocean (*Globigerina bulloides*). Measurements of their calcium isotopic composition ( $\delta^{44/40}\text{Ca}$ ) show variations of about 0.6 $^\circ/\text{oo}$  over the past 24 Ma. Both species fractionate Ca isotopes without a significant influence of temperature and can be used for the reconstruction of the Ca isotope composition of seawater ( $\delta^{44/40}\text{Ca}_{\text{sw}}$ ). The ( $\delta^{44/40}\text{Ca}_{\text{sw}}$ ) history calculated from *G. trilobus* and *G. bulloides* is in good agreement with previously published data (De La Rocha and DePaolo 2000) but exhibits more details due to a higher temporal resolution (ca. 1 Ma). Our records show an inverse correlation with seawater pH values, reconstructed from boron isotope ( $\delta^{11}\text{B}$ ) measurements on foraminifera from the same samples in the Equatorial Pacific Ocean (Pearson and Palmer 2000). There is, however, no correlation between  $\delta^{44/40}\text{Ca}_{\text{sw}}$  and  $\delta^{11}\text{B}$ . No current model gives a satisfactory explanation for the observed middle Miocene to Present long-term trend of combined rising  $\delta^{44/40}\text{Ca}_{\text{sw}}$  and falling pH. The Ca isotope trend could partly be explained by a decreasing oceanic calcium concentration, but only if the calcium concentration was reduced from 27 mmol/l in the middle Miocene to its modern value of 10 mmol/l. Short isotope and pH excursions in the early middle Miocene and Mid-Pliocene, lasting about 1-2 million years, may indicate input/output imbalances in the  $\text{CaCO}_3$  cycling of the ocean. References: De La Rocha, C.L. and DePaolo, D.J. (2000): Science, 289, 1176-1178. Pearson, P.N. and Palmer, M.R. (2000): Nature, 406, 695-699

## PP21C-1188 0830h POSTER

### Using Milankovitch Cyclicity as a High-Resolution Dating and Correlation Tool to Understand the Stratigraphic Evolution of the Late Neogene Central California Margin

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Natural gamma ray logs from Ocean Drilling Program (ODP) sites off the Central California margin and from oil wells on the outer continental shelf show cyclical variation at Milankovitch periodicities in the Neogene upper-Monterey and Sisuque Formations and their offshore equivalents. The well-dated ODP Site 1016, 150 km offshore of Point Conception, provides the basis for development of an orbital cyclicity-refined age/depth scale that can be applied to the mid-latitude North American margin region. We correlate silica-rich/detritus-rich cycles in logs from this site to cycles in more proximal offshore and onshore oil wells in a transect across the Santa Maria Basin, thereby helping to refine dating of these rapidly-accumulated, biostratigraphically-impoorished, fine-grained sediments, which are otherwise difficult to date. The higher resolution, orbitally-based age-depth scale provides refined dating of oil well logs, revision of the numerical age range of biostratigraphic markers, recognition and quantification of changes in sedimentation rates over time and in space, and identification of generalized climatic/sedimentation trends along the Alta-Baja California margin. For example: the new age model indicates that regional age ranges of some radiolarian biostratigraphic markers extend later than previously documented in other regions. Linear sedimentation rates decrease by an order of magnitude from 45-75 cm/ky to 7-8.5 cm/ky between proximal offshore locations and the distal Site 1016A. Analysis of the frequency modulation of the major harmonic in the frequency spectrum of the gamma ray vs. depth curve reveals the presence of condensed sections between 4.4-4.8 Ma and 5.3-5.6 Ma at Site 1016A. These two intervals may be associated with Neogene Hiatus 7 of Keller and Barron (1983). Natural gamma ray logs from deep-sea sites of ODP Leg 167 and the proximal Santa Maria basin wells show a similarity in gross secular trends along a 1300 km stretch of the Alta-Baja California margin, during the late Miocene to early Pliocene (7.0 to 3.5 Ma). Gamma ray count-inferred to reflect terrestrial detrital content—corresponds roughly with the broad rise and fall of eustatic sea level.

## PP21C-1189 0830h POSTER

### Links Between the Eastern Equatorial and Mid-Latitude Regions of the Eastern Pacific Ocean During the Pliocene-Pleistocene Transition

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The sustained warm period of the early Pliocene (4.6Ma to 3.1Ma) was the most recent period in the Earth's history when long-term equilibrium temperatures exceeded those of today. The subsequent continuation of the Earth's general cooling trend after 3.1Ma has been well documented, predominantly with records from the high latitudes of the Northern Hemisphere. The Pliocene - Pleistocene provides an excellent opportunity to better understand the importance of the connection between high latitudes and the tropical Pacific via the California and the Peru-Chile subtropical systems, during a major climate transition. We present the first comprehensive investigation of the role of the eastern Pacific Ocean in the Pliocene-Pleistocene transition using  $b^{18}O$  records of SST. ODP site 847 (0°12'N, 95°19'W, 3346m water depth) is located within the equatorial upwelling zone in the Eastern Equatorial Pacific (EEP) and serves as an excellent recorder of tropical Pacific climate dynamics. ODP site 1014 (32°50'N, 119°59'W, 1165m water depth) is located within the California Current (CC), and ODP site 1237 (16°0.4'S, 76°22.7'W, 3212m water depth) is located within the Peru-Chile current (PCC). These sites record both the strength of the eastern boundary currents in which they are located, which serve as a direct link between high and low latitudes via the advection of cold water, as well as changes in SST related to offshore upwelling. Sites 1014 and 1237 are

also indicative of conditions within the ventilated thermocline, an additional connection between the subtropical and tropical Pacific. Temperature records in both the tropic and subtropical Pacific show a gradual cooling trend, rather than a stepwise change at 2.75Ma often seen in northern hemisphere and ice volume records. Initial results indicate that the temperatures in the CC decreased by 8°C from 3 to 2Ma, and that modern conditions along the California margin were established by 2Ma. Temperatures in the EEP decreased by 3°C from 4Ma to the present, with increased variability in the last 1Ma. These results imply that reorganization in the tropical and subtropical Pacific was occurring before, during, and after the onset of major Northern Hemisphere glaciation, therefore making a tropical mechanism for increased northern hemisphere ice volume shift unlikely.

## PP21C-1190 0830h POSTER

### What Lies Beneath: 5 Million Year Record of Subsurface and Surface Ocean Conditions From the Eastern Equatorial Pacific Ocean

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Our results show that the Plio-Pleistocene (5.3 - 0.0 Ma) has been a period of dramatic change in the subsurface temperature and vertical structure of the Eastern Equatorial Pacific Ocean (EEP). We present records of subsurface and surface ocean temperature derived from magnesium calcium ratios (Mg/Ca) in foraminiferal calcite. Our estimates of absolute ocean temperature at the base of the photic zone (~100m) indicate a total cooling over the last 5 m.y. of approximately 10°C, occurring in two major steps. The first subsurface cooling, from ~19°C to ~14°C, occurred between 4.6 and 4.0 Ma and is not associated with a major change in EEP sea surface temperature (SST). The second subsurface cooling, from ~14°C to ~10°C, occurred between 2.5 and 0.0 Ma and is associated with an equivalent reduction in SST. We interpret a gradual trend in the carbon isotope composition of the subsurface dwelling foraminifera over the entire 5.3 Ma interval to indicate a change in the relative contributions of northern and southern sources to the thermocline in the EEP. Our estimates of subsurface ocean temperature are derived from Mg/Ca ratios in *Globorotalia tumida* (355-425 om) at Ocean Drilling Program site 847 (0°N, 95°W, 3347m water depth). Our SST estimates are derived from *Globoraminoides sacculifer* (w/o sac; 355-425 om) in the same samples. *G. tumida* has been shown in plankton tow and core top studies to occupy a relatively stable depth at the base of the photic zone (~100m in the EEP) while *G. sacculifer* has been shown to calcify predominantly in the mixed layer. Thus Mg/Ca ratios in *G. tumida* and *G. sacculifer* are a monitor of ocean temperature at these respective depths. We present a core-top calibration verifying the Mg/Ca-temperature relationship for *G. tumida* in the modern tropical Atlantic and Pacific oceans. The shift from a warmer (~19°C) to a cooler (~10°C) regime at 100m in the EEP has two possible causes. The first is an overall cooling of the subsurface driven by temperature changes in the subtropical northeast and southeast Pacific ocean, the regions that supply water to the EEP thermocline. The second is a shift in the depth of the thermocline from below to above 100m driven by changes in wind driven upwelling.

## PP21C-1191 0830h POSTER

### A Record of Oceanic Lithium Isotope Composition for the Last 7Ma

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Continental weathering plays an important role in global climate change but has proved difficult to reconstruct for the past. New geological tools with which to assess the past rate and style of weathering are therefore urgently required. One such tool is Li isotope fractionation. Recent studies [1,2] have shown preferential release of <sup>7</sup>Li into the aqueous phase and retention/adsorption of <sup>6</sup>Li during weathering processes such as partial dissolution and secondary mineral formation. Lithium behaves conservatively in the oceans, with a residence time of ~1Ma, so that a history of ocean Li isotope composition provides information about the average rate and style of global continental weathering on long timescales. The incorporation

of lithium as a trace element in marine carbonates enables the construction of a record of oceanic Li-isotopic variation and is the focus of this work. Carbonate Li-isotope compositions are lighter than seawater by ~8 per mil, but this fractionation is not temperature dependent. This has been demonstrated by measurement of Li isotopes in inorganically precipitated calcites (5-30°C) [3], in coralline aragonite (25-30°C) [3] and in benthic foraminifera *Uvigerina* (7-23°C). This lack of T-dependent fractionation suggests that the variation in the isotope composition of planktonic foraminifera will solely reflect changes in oceanic Li isotope composition, which in turn is strongly influenced by changes in continental weathering. ODP site 758, located on the Ninetyeast Ridge in the Indian Ocean (5°N, 90°E; 2925m), was sampled at 2m intervals, over a depth corresponding to the last 7Ma, to produce 55 samples with a temporal resolution of approximately 130Ka. Site 758 is previously well studied with an existing chronology and high resolution Sr, O and Nd isotope data. Individual foraminifera species in the core top were first investigated to assess inter-species fractionation effects. Down core lithium isotope variation was examined by measurement of hand picked and fully-reductively cleaned *G. menardii*. *G. menardii* was chosen because of its abundance throughout the core enabling the required 30-40mg of carbonate to be readily picked. Lithium isotope composition will be measured using a well established MC-ICP-MS technique [2,3] with a precision of better than ±1 per mil to provide a record of the Li isotope composition of seawater for the last 7Ma and to identify changes in continental weathering during this period. 1. Huh Y. et al. (2001) EPSL 194, 189-199. 2. Pistiner J. S. & Henderson G. M. (In press) EPSL. 3. Marriott C. S. et al. (2002) GCA S1 66, A485.

## PP21D MCC: 3004 Tuesday 1020h

### ITCZ Dynamics of Past Climates II (joint with A, H, OS, C, GC)

Presiding: A Koutavas, Massachusetts Institute of Technology; G Haug, GeoForschungsZentrum Potsdam

## PP21D-01 1020h

### Insolation-Driven Changes in Aridity Within the Amazon Basin Over the Last 40,000 Years

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Annual precipitation over the Amazon Basin is thought to be strongly linked to the average latitudinal position of the Inter-Tropical Convergence Zone (ITCZ). A more southerly ITCZ is considered to bring moisture to the Basin via the humid northeasterly trade winds, drawn in from the tropical North Atlantic. When the ITCZ is constrained further to the north these trades are restricted, and so the Basin should become more arid. Past changes in Amazon Basin hydrology therefore have the potential to monitor shifts in the palaeo-latitude of the ITCZ over northern South America. However, great debate surrounds the Pleistocene moisture history of the Amazon Basin largely due to the paucity of reliable, uninterrupted, regionally-representative proxy records back through the last glacial maximum (LGM). As a result, reconstructions are often highly-localised and based on qualitative indicators of change. On the other hand, material collected from the Amazon Fan (ODP Site 942) has allowed us to examine an average effective moisture signal from the whole of the Amazon Basin for the last