

## Timing of glacial changes in SST and $p\text{CO}_2$ from foraminiferal U/Ca, Mg/Ca and $\delta^{18}\text{O}$ in a Caribbean core

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One of the most critical tools for understanding the forcing of climate change is establishing the relative timing of changes in climate-related parameters such as sea-surface temperature, ice volume, salinity, and atmospheric carbon dioxide. Recently, the use of multiple geochemical proxies in foraminifers has emerged as a powerful technique for identifying changes in sea-surface temperature, ice volume, and salinity. Since these measurements are all based on the same sample, this approach improves the accuracy of leads and lags in timing by avoiding errors inherent in matching different age models (for example, for ice versus marine sediment cores) as well as ambiguities inherent in combining data from different sources (ie alkenone-based SST and foraminiferal  $\delta^{18}\text{O}$ ).

Here we use combined measurements of U/Ca and Mg/Ca in *G. ruber* from a Caribbean core (ODP999A) to examine the relative timing of changes in SST and atmospheric  $p\text{CO}_2$  at the end of the last glacial maximum and early deglacial period. Culture experiments have demonstrated that the U/Ca ratio in two species of planktonic foraminifera is inversely related to  $[\text{CO}_3^{2-}]$  in seawater. This region of the ocean is in equilibrium with atmospheric  $p\text{CO}_2$  today, and the *G. ruber* U/Ca record in ODP999A shows a remarkable resemblance to ice core  $p\text{CO}_2$ , consistent with a carbonate-ion control. Thus, a comparison of Mg/Ca (a proxy for SST) and U/Ca provides a means to examine the role of atmospheric carbon dioxide in forcing climate change. Our initial results confirm the ice core finding that within uncertainty, the increase in  $p\text{CO}_2$  (and therefore carbonate ion) is simultaneous with the increase in temperature at the end of the last ice age.

## High-resolution deglacial record of climate change in central Florida from fresh water ostracodes

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An 11.28 m sediment core was collected in Tampa Bay, FL, USA. During the last glacial period through the deglacial warming, the present day marginal marine system of Tampa Bay was a fresh water lake. Radiocarbon dates on well preserved shells, including nine during the deglaciation, provide a reliable chronology. Mg/Ca, Sr/Ca and  $^{18}\text{O}$  were measured on two species of freshwater ostracodes, *Limnocythere floridensis* and *Candona annae*. Variations in Sr/Ca reflect changes in water chemistry and Mg/Ca variations reflect changes in both water temperature and water chemistry. While absolute values were different for each species, the relative changes in Sr/Ca and Mg/Ca for both species were parallel.

Applying Sr distribution coefficients for *L. floridensis* (Chivas et al, 1986) and *C. annae* (Holmes and Chivas, 2002) results in virtually identical records of  $(\text{Sr}/\text{Ca})_{\text{water}} \cdot (\text{Sr}/\text{Ca})_{\text{water}}$  is relatively constant from 20 ka to 14.1 ka at 12.4 mmol/mol, increases by a factor of two from 14.1 to 12.5 ka to ~21 mmol/mol, then decreases by about 25% from 12.5 to 11.5 ka. High Sr/Ca values infer increased salinity due to higher evaporation during drier climates and vice-versa. Reliable Mg distribution coefficients as a function of temperature do not exist for these species so we can only infer relative temperature changes. The major trend is a doubling of Mg/Ca starting at 13.8 ka with a relative maximum at 12.5 ka, followed by a decrease of 30% to 11.5 ka. There is a 2.0% decrease in O-18 from 13.7 to 11.5 ka.

The overall scenario depicted by these proxies is a relatively cool and wet climate during the Bolling/Allerod from 14.3 to 13.8 ka, changing to a warmer and drier climate during the Younger Dryas, with the warmest period centered at 12.6 ka. This climate record from Central Florida is not synchronous with the northern high latitude ice core records and supports the observation that western tropical Atlantic SST was out-of phase with Greenland climate.

## The radiocarbon age glacial deep water

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Constraining the ventilation rate of the glacial ocean is important not only to climate studies but also to the understanding of temporal changes in the  $^{14}\text{C}$  to C ratio of atmospheric and upper ocean inorganic carbon. We are exploring one of the ways by which this might be accomplished; namely, by obtaining radiocarbon ages on coexisting benthic and planktic foraminifera shells. This approach is plagued by biases introduced by bioturbation, dissolution, and secondary radiocarbon addition. In order to avoid these biases, the measurements must be conducted on high deposition rate sediments and on more than one species of planktics. We will report a number of new results from cores in the western equatorial Pacific.

## Paired Mg/Ca and $\delta^{18}\text{O}$ records reveal mid Miocene paleoceanography

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Foraminiferal  $\delta^{18}\text{O}$  values are a function of temperature and the oxygen isotopic composition of seawater ( $\delta^{18}\text{O}_{\text{sw}}$ ), which reflects global changes in the amount of freshwater frozen at the poles and regional precipitation versus evaporation patterns. Using foraminiferal Mg/Ca ratios as an independent temperature constrain in conjunction with  $\delta^{18}\text{O}$  values affords the opportunity to derive the  $\delta^{18}\text{O}_{\text{sw}}$  from which changes in global ice volume can be inferred assuming that regional changes in  $\delta^{18}\text{O}_{\text{sw}}$  are minor.

In this study we set out to apply this approach to constrain the magnitude of the second major ice expansion event on Antarctica between about 15-13 Ma. We measured Mg/Ca ratios and  $\delta^{18}\text{O}$  values on benthic foraminifera from western subtropical Pacific Deep Sea Drilling Program Hole 588A spanning 11-16 Ma with a temporal resolution of 30 kyr.

Our results show unexpectedly large Mg/Ca variations of between ~2 and 4 mmol/mol. The ratios are too high to be a function of intermediate water temperatures. Mg/Ca maxima and minima follow the same long term trend making it unlikely that the data are entirely artificial (e.g., diagenetic overprints or clay contamination). The long-term temperature and corresponding  $\delta^{18}\text{O}_{\text{sw}}$  trends parallel the long-term trend in the Southern Ocean record of *Shevenell et al.* [2004]. At both sites, there is a pronounced temperature maximum ~14.5-14.4 Ma postdating minimum foraminiferal  $\delta^{18}\text{O}$  values by ~0.5 myr. The corresponding  $\delta^{18}\text{O}_{\text{sw}}$  values exhibit a maximum concurrent with this temperature maximum, but predate the foraminiferal  $\delta^{18}\text{O}$  maximum at 13.8 Ma by ~0.6 myr. We do not believe that the  $\delta^{18}\text{O}_{\text{sw}}$  maximum reflects ice extent. It would imply maximum glaciation during the time of warmest surface and intermediate water temperatures. Rather, the coincidence of a temperature maximum in surface and intermediate depth waters and high water mass  $^{18}\text{O}/^{16}\text{O}$  ratios points to a change in the isotopic composition of high latitude surface and intermediate water during a climatically warm interval. These observations demonstrate the importance of regional water mass effects on the oxygen isotopic composition of foraminifera.

### Reference

Shevenell, A. E., Kennett, J. P. and Lea D. W. (2004), *Science*, **305**, 1766-1770.

## Carbonate paleothermometry based on abundances of $^{13}\text{C}$ - $^{18}\text{O}$ bonds

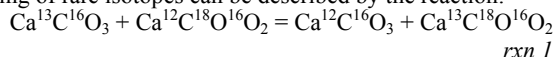
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Urey's carbonate oxygen isotope paleothermometer is a milestone of paleoclimate research but constrains temperature only if the oxygen isotope composition of water from which carbonate grew is known. Moreover, difficulty in recognizing diagenetic overprinting has confounded the interpretation of carbonate oxygen isotope compositions for much of the geological record. We present a carbonate paleothermometer based on the formation of bonds between  $^{13}\text{C}$  and  $^{18}\text{O}$ . This ordering of rare isotopes can be described by the reaction:



The equilibrium constant for rxn. 1 is temperature dependent and constrained by the isotopic composition of carbonate alone. Experiments on carbonate standards demonstrate that this equilibrium constant can be measured by phosphoric acid digestion and analysis of the proportion of  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$  in product  $\text{CO}_2$ .

Calcite inorganically precipitated from aqueous solution at 323-273 K has a 0.56-0.75 ‰ excess of  $\text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$  relative to the amount expected for a random distribution of isotopes, and this excess is positively correlated with  $1/T^2$ . These results are broadly consistent with theoretical models of the energetics of rxn. 1. Given the external precision of our measurements (ca. 0.01 ‰), it should be possible to use rxn. 1 to do paleothermometry with uncertainties as low as ca.  $\pm 1^\circ\text{C}$ .

Analyses of recent surface and deep-sea corals yield abundances of  $^{13}\text{C}$ - $^{18}\text{O}$  bonds that are consistent with their known growth temperatures, based on our experimental calibration of rxn. 1. These corals are aragonitic and have variable, sometimes large, 'vital effect' contributions to their  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. Thus, the success of our measurements suggests vital effects and structural differences between calcite and aragonite have small or negligible effects on the equilibrium constant of rxn. 1.

We will present the results of an application of the  $^{13}\text{C}$ - $^{18}\text{O}$  thermometer to late-preCambrian limestones and dolomites from Namibia and the Canadian Cordiera.

## Unraveling nutrient, growth rate, calcification, and diagenesis effects on the chemistry of coccolith calcite

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Coccoliths are the dominant biogenic carbonate in many deep sea sediment cores, and recent work to constrain the influence of vital effects on coccolith stable isotopic measurements, and to exploit vital effects on Sr/Ca ratios in coccoliths, have renewed interest in proxies from coccolith chemistry. Coccolith Sr/Ca ratios are correlated with productivity across upwelling gradients and in some transient blooms. To assess whether this response is triggered by cell growth and calcification or nutrient availability, and whether different responses among different genera reflect different ecological responses to these environmental gradients, we analyze Sr/Ca ratios of different coccolith fractions from a series of sediment traps in the northern and southern Bay of Bengal. In the northern trap series close to major river deltas, maximum coccolith fluxes occur during the southwest summer monsoon when productivity is highest, and correspond to elevated Sr/Ca ratios in several species. In some species, Sr/Ca ratios are more correlated to total productivity than to the export flux of coccoliths from that species, suggesting a link to an environmental variable like nutrients, or export response truncated by grazing. We further evaluate the nutrient influence on Sr/Ca with analysis of coccolith chemistry in N-limited and P-limited chemostat cultures of coccolithophorid *Emiliana huxleyi*.

New ion probe techniques for Sr/Ca measurements on individually picked coccoliths isolate the Sr/Ca variations in single species of fossil coccoliths from sediments. This approach reveals a large heterogeneity of Sr/Ca ratios among different genera of coccoliths. Such heterogeneity suggests that diagenesis has not homogenized the Sr/Ca ratios of coccoliths in many older (in this case Paleocene) sediments, an asset for paleoreconstructions. However, it indicates that the elemental variations in bulk carbonate may be influenced by changing nanofossil assemblages.

## Foraminiferal lithium as a paleoceanographic proxy

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Lithium in foraminiferal carbonate shows great potential as an indicator of environmental change over both long and short timescales. The dissolved lithium concentration and isotopic composition of seawater is controlled by rates of hydrothermal interaction with oceanic crust and continental weathering/riverine input, assuming the fractionation factor for the removal processes has remained constant. The lithium isotopic composition of planktic foraminifera (*Orbulina universa*, *Globigerinoides sacculifer*, *Globorotalia menardii*, and *Globorotalia truncatulinoides*) resembles seawater, such that the isotopic fractionation from the precipitation of foraminiferal calcite appears to be minimal. Therefore, differences in foraminiferal  $\delta^7\text{Li}$  can reflect fluctuations in hydrothermal and continental weathering rates over million year timescales. For example, data from the mid-Cretaceous (122-98 Ma) shows a decrease in foraminiferal  $\delta^7\text{Li}$ , suggesting that hydrothermal activity across the Aptian-Albian boundary increased and altered seawater chemistry. This interpretation is supported by changes in microfossil assemblages, a  $^{87}\text{Sr}/^{86}\text{Sr}$  minimum, and a significant decrease in foraminiferal Mg/Ca.

Foraminiferal Li/Ca ratios across glacial/interglacial cycles have been invoked as a proxy for changes in seawater carbonate ion concentration. Li/Ca offers two advantages over other trace element proxies in this regard: First, lithium is conservative in the ocean in that it does not significantly interact with the biological cycle. Therefore, lithium incorporation is not dominated by changes in nutrients or biological productivity. Further, lithium has a relatively long residence time compared to bioactive elements such as zinc. As such, short-term Li/Ca records are anticipated to change in response to paleoenvironmental conditions rather than ocean lithium concentrations. On longer time scales (over millions of years) foraminiferal Li/Ca can provide a record of secular changes in seawater lithium concentration. Culturing studies are currently underway to isolate the influence of carbonate ion concentration and other growth conditions on foraminiferal Li/Ca incorporation.

## New insight into the utility of carbonate-associated sulfate

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Carbonate-associated sulfate (CAS) occurs at ppm levels in many modern and ancient limestones and dolostones. There is a growing body of evidence confirming that coeval seawater sulfate-S isotope relationships are faithfully preserved in CAS. More recently, careful acid extractions have yielded CAS also suitable for oxygen isotope analysis. For example, modern muds in Florida Bay record the oxygen isotope composition of overlying seawater sulfate, even in settings of pronounced diagenetic sulfate reduction and calcium carbonate precipitation. Although we are careful to use buffers to minimize pH-dependent isotopic exchange, we are exploring the full sensitivity of oxygen isotopes to the CAS procedure. Through these oxygen analyses, we hope to uniquely capture the sources of sulfate to the early ocean as continental weathering fluxes and seawater sulfate concentrations increased with increasing biospheric oxygenation. Oxygen in sulfate provides a unique window on the environments of sulfide oxidation and the internal biogeochemical cycling of S once delivered to the ocean.

CAS concentrations vary dramatically in modern and ancient carbonates, but Precambrian samples are consistently depleted relative to Phanerozoic counterparts. Rather than being entirely a product of diagenetic resetting, our results suggest that primary trends, if not absolute values, are preserved in the concentration data. Nevertheless, the coralline Pleistocene Key Largo Limestone reveals concentrations that decrease by almost an order of magnitude with transformation of aragonite to calcite under meteoric conditions, highlighting the caution necessary in any interpretation of CAS concentrations. Not surprisingly, the S isotope data are buffered to near-seawater values across this transition. We are currently exploring the effects of modern dolomitization, although past comparisons of interbedded Proterozoic gypsum and dolomite suggest that S isotope integrity can be preserved at least during early dolomitization. We are also now able to measure low CAS concentrations via ion chromatography following near-complete removal of the interfering chloride matrix. Most recently, our CAS analyses across pronounced C isotope excursions in the Paleozoic are revealing patterns of rapid isotopic variability previously described only from the Proterozoic.

## A critical review and recent advances in the boron isotope paleo-pH proxy

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Proxy development inevitably involves an initial success where a simple application seems to work perfectly, followed by many years of investigating the complications. After 16 years, the boron isotope paleo-pH proxy remains promising if carefully applied. It is clear that the first order control on the boron isotope composition of marine calcium carbonate is the pH of seawater. Other influences such as temperature, pressure, salinity, alkalinity, kinetics (vital effects and life cycle influences, precipitation rate), and preservation (diagenesis) need to be understood to use the proxy with confidence. Premature applications without consideration of these factors (as well as data quality), has only complicated proxy development.

Our group has focused on ground-truthing through survey studies of modern marine carbonates, core top studies<sup>1</sup>, culture experiments under controlled conditions (foraminifera and corals<sup>2</sup>), and synthetic carbonate mineral growth experiments (in progress). Core top studies have shown previously unknown dissolution and shell size effects which can be avoided with careful sample selection. With this knowledge, surface ocean pH (and aqueous PCO<sub>2</sub>) has been confidently determined in late Quaternary samples where the isotope composition of seawater can be assumed constant. A remarkable covariation of the foraminiferal boron isotope composition with climate records of atmospheric pCO<sub>2</sub> and marine oxygen isotopes bears this out.

### References

- [1] Hönisch, B. & Hemming, N.G. (2004). *Paleoceanography* **19**. doi:10.1029/2004PA001026
- [2] Hönisch, B. et al. (2004). *Geochim. Cosmochim. Acta* **68**. 3675-3685.

## Isotopes in Paleozoic carbonate components: An evaluation of proxies

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Brachiopods, trilobites, cement and whole rock were evaluated for their reliability as proxies of original seawater carbon, oxygen and strontium isotope chemistry. Coeval material was evaluated from horizons of formations spanning the Permian to Cambrian.

Unaltered shells of low-Mg calcite articulated brachiopods retain original seawater oxygen, carbon and strontium isotope compositions, as old as late Ordovician. Assessments of older specimens are hampered by a lack of suitable material (coeval brachiopod-whole rock sets). A definitive assessment of cement marine chemistry is difficult due to the paucity of material, but despite this caveat, cements hold some promise for retaining original carbon and possibly strontium isotope seawater values. The potential of whole rock material as a proxy of original seawater chemistry is quite complex. In some, but not all instances, the carbon isotopic composition of whole rock, after detailed scrutiny and evaluation, appears to represent an original seawater chemistry signal. In few instances their oxygen isotope compositions reflect original seawater values. Unlike the stable isotope compositions, strontium isotopes of all studied whole rock material (Permian to upper Cambrian) do not reflect original seawater chemistry values. Thus the potential for retaining original seawater isotope chemistry and serving as proxies, in order of decreasing reliability, are 1) unaltered low-Mg calcite brachiopods (C, O & Sr isotopes), 2) pristine marine cements (C & Sr isotopes), and 3) whole rock material (C isotopes ?).

Carbon, oxygen and strontium isotope compositions of Ordovician trilobites mirror those of coeval unaltered brachiopods. Cambrian trilobites hold significant promise as an important proxy of original-seawater isotope chemistry but further studies are needed to ascertain their full potential. The survey of isotopes in some Ordovician and Cambrian intermediate/low-Mg calcite trilobites demonstrates their potential as an important proxy of original seawater chemistry.

## Isotopic evidence for shallow-water carbonate dissolution and reprecipitation

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In shallow water carbonate sediments of the Bahama Banks, distinct differences in pore water  $\delta^{13}\text{C}$ -dissolved inorganic carbon (DIC) profiles in the upper 20 cm of sediment were observed at dense and intermediate density seagrass sites and in bare (no seagrass) oolitic sands.

Isotope mass balance calculations were used with these results to estimate the  $\delta^{13}\text{C}$  of the DIC being added to these pore waters. At intermediate seagrass sites and in bare oolitic sands, these results indicate that there is a 1:1 mixing of DIC from the coupling of organic matter (OM) remineralization and sediment carbonate dissolution ( $\text{CH}_2\text{O} + \text{O}_2 + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ ). These isotope results also indicate that the source of OM undergoing remineralization is seagrass OM at the intermediate seagrass sites and is detrital OM in the bare oolitic sands.

In contrast, similar calculations for dense seagrass sites suggest that the DIC being added to these pore waters is too heavy, having a  $\delta^{13}\text{C}$  value of  $+2.4 \pm 0.3\%$ . Based on the reaction above this predicts that the OM undergoing remineralization has a  $\delta^{13}\text{C}$  value of  $+0.5 \pm 0.6\%$ , a value that is inconsistent with any known sediment OM sources.

However, these data may be explained if carbonate reprecipitation occurs along with OM remineralization and carbonate dissolution. Since metastable high-Mg calcite appears to be the dominant phase dissolving in these sediments, reprecipitation of more stable low-Mg calcite or aragonite may occur along with dissolution of high-Mg calcite. Since the reprecipitated carbonate is isotopically lighter than the original carbonate that dissolves, the DIC added from OM remineralization and net dissolution (dissolution minus reprecipitation) becomes heavier.

Simple closed system calculations with a reprecipitation/net dissolution ratio of  $\sim 7$  (consistent with field results from Florida Bay) predict a value for the  $\delta^{13}\text{C}$  of the DIC being added to pore waters (in a net sense) that is consistent with our results from dense seagrass sites.

The occurrence of this type of recrystallization has important impacts in terms of understanding sediment diagenetic processes and their impact on the evolution of carbonate platforms such as the Bahama Banks. These results may also be important in terms of the interpretation of the  $\delta^{13}\text{C}$  paleoceanographic records on such platforms.

## Carbon and oxygen isotopic characteristics of carbonate rocks of carboniferous-permian in Jiangshan, Zhejiang Province, China

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The studied carbonate rocks were collected from Chuanshan Formation and Qixia Formation at the Shitoushan section in Jiangshan, Zhejiang Province, China. Variation range of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are respectively  $-5.4\%$ – $-4.4\%$ ,  $-12.2\%$ – $-5.6\%$ , and their average are  $0.49\%$  and  $-8.37\%$ , respectively. No obvious shift of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  is found near the borderline between Carboniferous and Permian. The carbon isotopes curve of the strata coincides with the variation curve of sea level inferred from sedimentary facies. The deepening of sea-water conforms to the peak of  $\delta^{13}\text{C}$  value. Variation rule of sea water in the section is from shallow, middle, deep to middle, accordingly the evolution curve of  $\delta^{13}\text{C}$  is from trough, relatively flat with sub fluctuation, wave peak to flat. The sea level evolution curve inferred from strata record in the studied area rises gradually and doesn't coincide with the global change curve of sea level [1], which is probably the result of settlement of Zhejiang - Anhui sea basin. The phenomenon is proved also by record of carbon isotope. Value of  $\delta^{13}\text{C}$  rose gradually, and then decreased slightly in the last from the late of Late Carboniferous to the early of Early Permian. The evolution curve of carbon isotopes doesn't coincide with that from Veizer *et al.* (1986) [2]. Therefore, the evolution curve can reflect the evolution of regional crust in some degree.

### References

- [1] Vail P R, Mitchum R.M, and Thompson S. (1974) *Geol. Soc. Am. Abstr. Prog.* **6-7**, 63-82.
- [2] Veizer J, Fritz P, Jones B. (1986) *GCA* **50**, 1679-1696.

## Latitudinal gradient in $\delta^{18}\text{O}$ of Permian brachiopods

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Oxygen isotope values of calcareous shells of articulated brachiopods are often utilised to estimate paleoseawater temperatures because the secondary layer of these organisms are rather resistant to diagenetic alteration, and the degree of alteration can be evaluated by optical and chemical techniques [e.g., 1, 2]. Although, Auclair et al. [3] in one modern intertidal specimen observed deviations of several permil for oxygen isotopes, the norm for the secondary brachiopod layer are  $\delta^{18}\text{O}$  values mostly within  $\pm 1\%$  of isotopic equilibrium with ambient seawater [4, 5].

Here we present new oxygen isotope data of Permian articulated brachiopods from Pakistan and Australia which were deposited at latitudes greater than  $45^\circ\text{S}$ . These high-latitude brachiopods were compared to coeval low latitude and warm water counterparts [2]. The  $\delta^{18}\text{O}$  values of high-latitude late Permian brachiopods from Pakistan are between  $-1.0$  and  $-3.0\%$ , and, on average, are  $0.8\%$  heavier than coeval low latitude counterparts. Calculated temperatures of Permian seawater of Pakistan were on average  $3\text{--}4^\circ\text{C}$  cooler than that of coeval low latitudes. The high-latitude Australian brachiopods yield oxygen isotope values ranging from  $+1.0$  to  $-2.6\%$ . These values are about  $2.0\%$  heavier than those of their low latitude counterparts suggesting that high latitude paleoseawater was up to  $9^\circ\text{C}$  cooler. Moreover, the temporal early Permian melting of continental ice and consequent ice-volume impact on the oceans of about  $2.0\%$   $\delta^{18}\text{O}$  documented by low latitude brachiopods [2] is also observed by their high latitude counterparts.

The Permian brachiopod datasets demonstrate for the first time significant differences in oxygen isotope values between low and high latitude seawater.

### References

- [1] Veizer et al. (1999) *Chem. Geol.* **161**, 59-88.
- [2] Korte et al. (in review) *Palaeogeogr. Palaeoclimatol.*
- [3] Auclair et al. (2003) *Chem. Geol.* **202**, 59-78.
- [4] Carpenter and Lohmann (1995) *GCA* **59**, 3749-3764.
- [5] Brand et al. (2003) *Chem. Geol.* **198**, 305-334.

## Oxygen isotope exchange between calcite and water: An experimental study

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Analysis of oxygen isotope composition in carbonate fossils is a widely used method to quantitatively estimate palaeotemperatures. Considerable information about oxygen isotope fractionation between calcite and water already exists in the literature but there is still no consensus on equilibrium fractionation magnitude and on the role of calcite precipitation rate. The aim of this work was to study oxygen isotope fractionation between water and precipitated calcite under strictly controlled experimental conditions. Precipitation experiments were carried out using the constant addition technique at  $25^\circ\text{C}$ .

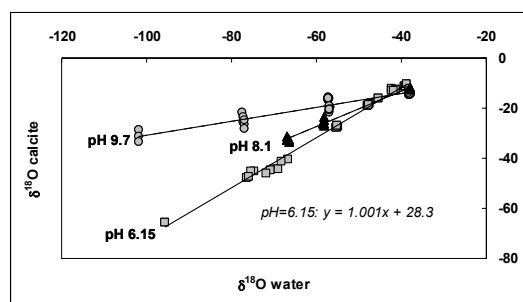


Fig 1 shows the equilibrium relation between calcite and water  $\delta^{18}\text{O}$  compositions at different pH.

1) the lines have nearly one intersection point ( $\delta^{18}\text{O}_{\text{cc}} \sim -14\%$ ) that corresponds to  $\delta^{18}\text{O}$  of  $\text{Na}_2\text{CO}_3$  in the source input solution;

2) the slope of the lines representing fraction of isotopic exchange increases as pH decreases and approaches 1 (equilibrium) at pH close to 6;

3) line with the slope 1 corresponds to the value  $\Delta_{(\text{cc-w})} \approx 28.3\%$  that is very close the equilibrium value.

Dis-equilibrium at higher pH means that calcite precipitation outpaces oxygen isotope equilibration with water, that is, precipitation is fast enough that  $\text{CO}_3^{2-}$  units in the crystal are buried before they isotopically equilibrate with  $\text{H}_2\text{O}$ . Because the calcite surface is largely equilibrated isotopically with  $\text{CO}_3^{2-}$  in the solution, isotope equilibration is likely prevented by slow isotopic exchange between dissolved  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{O}$ .

## Methane-derived carbonates of the Nankai Trough in southeast Japan: Are they related methane hydrates?

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Fore-arc basin sediments of the Nankai trough is characterized by methane seeps and seep-related phenomenon such as mud volcano and precipitation of authigenic carbonates. Considering the distribution of methane hydrate in the Nankai trough, methane seeps are suspected to be related with methane hydrates. A number of carbonate samples were collected by grabs or piston corers during the GH cruises in 2002, 2003, and 2004. Authigenic carbonates occur either as "chimney"-like cylindrical shape, 25 cm across and 42 cm high, and thick massive bed with occasional shell fragments, ~60 cm thick.

XRD measurement of carbonates has revealed that almost all carbonates are predominated by high-magnesian calcite with some pyrite and very few dolomite. Mg content of calcite exceeds 10 mol.% (Chen, 2005). The  $\delta^{13}\text{C}$  values range between -31.2 and -37.3 permil PDB, which indicates that the precipitation of calcite is related with the methane oxidation. Sulfate concentration of the pore waters is observed to decrease with burial, indicating the depth of SMT (Sulfate-methane transition) at around 10 to 15 m below seafloor (Matsumoto, et al., 2005). Sulfate-reduction by methane increased  $[\text{HCO}_3^-]$ , alkalinity and the activity of free  $\text{Mg}^{2+}$  within sulfate reduction zone. These process caused the precipitation of high Mg-calcite.

Methane is generated either through microbial or abiotic thermogenic processes; the former is characterized by relatively light carbon (< -60 permil PDB) whereas the later, by heavier carbon (> -50 permil PDB). Assuming that the carbon in authigenic carbonates is mostly from methane, the Nankai trough carbonates are thought to have been derived from thermogenic methane. However, methane of gas hydrate in the Nankai trough is microbial methane (Waseda et al., 2004). This seems to suggest that methane-bearing cold seep in the Nankai trough is not directly related with subsurface methane hydrate.

### References

- Waseda A., et al., 2004, *Resource Geol.* 54(1), 69-78.  
Chen Y.F., 2005, PhD Thesis (University of Tokyo).  
Matsumoto R., et al., 2005, *Geochem. Explor.* (submitted).

## Ce anomaly of carbonate rock as a geochemical tracer for redox conditions of paleo-atmosphere

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The atmospheric evolution is one of important parts in the Earth System Model. The timing of oxygenation of global atmosphere has been a most controversial issue: the gradual increasing C-W-K-H model vs the constant oxic D-K-O model as summarized by Ohmoto (1997).

Fryer (1977) first suggested 0.8-1.9Ga as the increasing period of atmospheric oxygen based on Eu and Ce anomalies signatures in Precambrian BIFs. The complication of BIF forming condition resulted in severe criticism and argument.

Carbonate sediments are commonly considered to be formed in a shallow seawater which was in equilibrium with contemporary atmosphere in oxygenation condition. The pure carbonate rocks recorded the REE patterns of seawater in which they formed. And the REE are immobile during diagenesis and metamorphism we assumed.

Over 70 rather pure carbonate rocks of Precambrian from China, South Africa and Australia have been analyzed by means of the INAA in Washington University and the ICPMS in both Chinese Geochemistry Institutes. Most of young carbonates show similar REE patterns of present river and sea waters with negative Ce anomalies, while most of old ones with no Ce anomaly. It indicates that the oxygenation conditions of paleo-atmosphere has been changed from redoxatmoversion to oxyatmoversion. The changing period might be around 1.9 Ga. This result is in good agreement with the gradual increasing C-W-K-H model of atmospheric oxygen evolution, and also with conclusion from other evidence of geological clues, such as the developments of the BIF, red beds, Au-U conglomerates and carbon isotope excursion event.

There were some exceptional samples for this regularity caused by local precipitation environment. More global sampling, especially for those around the changing period, is essential to refine the scale of atmospheric oxygen evolution.

### Acknowledgements

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## **Cadmium enrichments in Jurassic carbonates: Causes and mechanisms**

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Marine carbonate rocks represent a widespread lithology hitherto thought to be depleted in cadmium (Cd), a highly toxic trace metal that is transferred into the environment by weathering processes. However, we have identified middle and lower upper Jurassic carbonates outcropping in Switzerland, France, Spain and Italy as being considerably enriched in Cd, independent of their particular facies and correlated in time. Moreover, in one of the sections studied (Terminilletto/I), a positive correlation between Cd enrichments and the carbon isotope record has been observed.

The widespread occurrence of Cd anomalies in Jurassic carbonate rocks in western Europe and its correlation with the stable carbon isotope variations suggest that this enrichment was associated with a general change in the Cd cycle in the western Tethyan realm, probably related to contemporaneous global environmental changes that induced variations in the seawater composition. In this context, a direct incorporation inside the calcite lattice during carbonate precipitation is probable, although Cd transfer into carbonates during early diagenesis is also possible. Both experiments of sequential extraction (ICP-MS analyses) and maps of Cd repartition (micro X-Ray fluorescence analyses), that are underway, will allow us to better constrain the Cd bearing mineral phase and help us to elucidate the mechanism of Cd incorporation into carbonate rocks.

## **Systematic spatial variations of Ba and Sr enrichments over ambient seawater values in saline, geothermal, submarine springs on the West Florida Shelf**

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Several saline, geothermal, submarine springs are known to occur on the West Florida Shelf, at depths of 17-23 m and about 10 miles off shore. These have been shown to emit a constant flow of warm, saline water ( $t = 33 - 36$  °C;  $S \sim 35$ ), containing micromolar levels of sulfide. A model devised in the late 1960s proposes that seawater penetrates the Florida Plateau, most likely around the Florida Straits. This seawater is geothermally heated to a temperature of about 42 °C as it flows at 800 – 1000 m depth toward the axis of the Florida Plateau—roughly coinciding with the southern section of the West Florida Shelf—where it finally rises to the surface and emerges from a multitude of separate vents. This system is a rare example of warm seawater interacting extensively with a massive carbonate platform, rather than igneous rocks.

Detailed studies in the late 1970s revealed that the spring effluents have compositions nearly identical to that of seawater, except for distinct Ca enrichments and Mg depletions probably resulting from dolomitization. The effluents are also highly enriched in Ra. During annual visits from 1996 to 2003, we collected high-purity effluent from four springs, using a syringe sampling technique performed by SCUBA divers. Filtered effluent was analyzed for major ions by ion chromatography and for Sr and Ba by ICP-MS. Major ion analyses confirm the seawater-like character of the effluents, as well as the Ca enrichment and Mg depletion. The alkaline earth elements Sr and Ba, like Ca and Ra, are enriched in the effluents by factors of 1.5 – 4 and 4 – 6, respectively. These Sr and Ba enrichments, while extremely stable over the 7-year sampling period, increase systematically from south to north, which may be indicative of the progressive interaction of warm seawater with the carbonate substrate, and hence of the direction of its flow deep underneath the Florida Plateau. Combined with a previous estimate of the flow rate from a single vent (~25 L/s), these results suggest that the springs may impart a pronounced chemical and thermal imprint on the coastal seawater of the West Florida Shelf.

## Elemental remobilization in marine sediments: Growth and destruction of authigenic mineral fronts above gas hydrate systems

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Microbial oxidation of dissolved methane in marine sediments often leads to depletion of dissolved sulfate and an abrupt change in alkalinity. We present data from Blake Ridge (ODP Leg 164), the Peru Slope (ODP Leg 201), and the Japan Sea (Cruise UTO4) where long-term oxidation of methane has produced pronounced authigenic fronts within the sediment column as a result of this process. These fronts are produced as a result of supersaturation with respect to the carbonate minerals and barite. Without exception, major fronts are closely associated with the present zone of sulfate-methane transition (SMT), indicating that they are part of an ongoing dynamic process and do not represent relicts of previous depositional events. The depth profiles of pore fluids also indicate a corresponding response to microbial sulfate reduction as the predominant oxidative process in shallow sediments. The depth of the SMT in the three study areas ranges from as little as 2m in the Japan Sea study area to as great as 20m in the Blake Ridge.

In order for the authigenic fronts to persist as discrete intervals within the SMT, precipitation at the top of the fronts must be countered by dissolution of the lower portions as they are buried. Over time, the diffusive return of solutes to zones of saturation leads to the growth of these fronts. Based on present flux of dissolved calcium, barium and strontium, the accumulation of barite and carbonate fronts spans over tens of thousands of years. Similarities between data from distinct localities support the hypothesis that the upward diffusion of methane on continental margins is both regionally ubiquitous and temporally nonephemeral.

## Impacts of Fe-rich sediment input upon chemical diagenesis of shallow marine tropical carbonates: Discovery Bay, Jamaica

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The chemical dissolution of skeletal carbonate grains has been identified as a significant diagenetic process in shallow water, tropical carbonate sediments. Such dissolution is associated with acidity produced through the oxidation of sulfide generated during bacterial sulphate reduction. It is to be expected, however, that the presence of Fe, introduced through terrigenous input, will significantly modify chemical diagenesis. High Fe levels should promote bacterial Fe(II) reduction, minimising sulfide production and subsequent oxidation. In order to test the effects of Fe-rich sediment input we have examined sites in Discovery Bay, Jamaica, a carbonate-dominated embayment in which some areas have been subject to the input of Fe-rich bauxite dust since 1965.

Cores from non-impacted ('clean') areas of the bay show evidence for active sulphate reduction in the upper 10cm of the sediment column. Associated petrographic and SEM observations of carbonate grains (specifically *Halimeda* and *Amphiroa*) show clear morphologic evidence of chemical dissolution. In contrast, cores from sites subject to significant bauxite sediment inputs (up to 7500 ppm Fe) show evidence of active iron reduction in the top 10cm of the sediment column, with no evidence of active sulphate reduction. Carbonate grains from these same sites show little evidence for active dissolution and are characterised by often pristine surface morphologies. The implications of such shifts in chemical diagenesis as a result of Fe-rich sediment input are far-reaching. Inhibition of grain dissolution will result in better grain assemblage preservation, and greater preservation of primary isotopic and chemical compositions.

## **A paleoceanographic model for the Michigan Basin during silurian time from stable isotopic analysis of brachiopods**

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Stable C and O isotopic analyses of microsampled brachiopod shell material from the middle Silurian Burnt Bluff Group has established fundamental information on the paleoceanographic conditions in the Michigan Basin during the Silurian. These data indicate that, despite clear lithological evidence for highly restricted conditions at times during the Silurian, the Michigan Basin was also characterized by periods of normal marine circulation.

The Michigan Basin was an equatorial depocenter during Silurian time. Fluctuations between normal marine conditions indicated by periods of luxuriant reef growth coupled with deposition of restricted marine facies and evaporites are especially prevalent during the Silurian. Little geochemical evidence exists, however, to establish the timing and magnitude of variability in paleoceanographic conditions within the basin

Non-altered pentamerid brachiopod shells have average isotopic values of  $-4.50 \pm 1.0\%$  ( $\delta^{18}\text{O}$ ) and  $+1.21\% \pm 0.99$  ( $\delta^{13}\text{C}$ ). Other time-equivalent datasets from open marine basins in Eurasia and North America show similar  $\delta^{18}\text{O}$  values to those of this study, indicating that the Michigan Basin was also open to normal marine circulation. In addition, microsampling transects parallel to growth lines allows the reconstruction of isotopic patterns during the growth of the animal. In some specimens, covarying trends in O and C isotopes were observed to have a cyclic pattern, which may be a result of changes in productivity related to seasonal patterns.

Establishing isotopic conditions of marine waters in the Michigan Basin provides additional data points for the composition of normal Silurian seawater for comparison with other basins, while also shedding new insight into the circulation patterns within the Michigan Basin.