

Controls on paleo-alkenone $\delta^{13}\text{C}$

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The carbon isotopic fractionation that occurs during marine photosynthetic carbon fixation (ϵ_p) is primarily a function of surface-water $[\text{CO}_{2\text{aq}}]$, growth rate, and cell geometry. Although modern data suggest that haptophyte growth rates exert a dominant control on the value of $\epsilon_{p37.2}$, some patterns of paleo- $\epsilon_{p37.2}$ change are contrary to changes in nutrients inferred from foraminiferal trace element concentrations. Further, comparison of $\epsilon_{p37.2}$ values for the past ~45 million years with $\epsilon_{p37.2}$ values from modern growth environments, spanning oligotrophic to eutrophic sites, indicate that changes in algal growth rate is not the first-order control on the long-term trend. If changes in cell geometry of alkenone-producers were minimal, then long-term trends in $\epsilon_{p37.2}$ qualitatively reflect a decrease in $[\text{CO}_{2\text{aq}}]$ from the middle Eocene to the early Oligocene. Atmospheric carbon dioxide concentrations can be estimated using the modern calibration for $\epsilon_{p37.2}$ as a function of surface-water $[\text{PO}_4^{3-}]$ and $[\text{CO}_{2\text{aq}}]$, assuming the range of paleo- $[\text{PO}_4^{3-}]$ for each site was similar to modern distributions. This approach yields middle Eocene $p\text{CO}_2$ levels ~3 to 5 times that of modern levels. $p\text{CO}_2$ rapidly declined following the Eocene/Oligocene boundary reaching modern concentrations near the end of the Oligocene.

Recent measurements of coccolith geometries suggest changes in algal geometries of alkenone-producing algae did occur. These results and their impact on carbon dioxide estimates will be discussed.

The importance of a vital effect on the Ca isotopic composition of foraminiferal tests

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The influence of temperature on Ca isotope fractionation during biomineralisation was investigated through the paired analyses of $\delta^{44/42}\text{Ca}$ (via MC-ICP-MS) and $\delta^{18}\text{O}$ on the calcite tests of twelve species of planktonic foraminifera from core-top sediments [1]. No significant correlation between temperature and Ca isotopes was observed in any of the twelve species of foraminifera investigated. The results suggest that the theoretically-expected relationship [2-3] between Ca isotopes and temperature can be obscured by, as yet, unquantified metabolic and physiological processes in nature. Variable growth-rate could be a reason for this vital effect [3] but cannot explain inter-species variations. Vital effects on Ca-isotopes are particularly relevant to the globorotaliid species and *G. bulloides* in core-top studies but could also explain the discrepancy between laboratory-determined temperature calibrations and core-top data for *G. sacculifer* [4]. It is doubtful that the effects of metabolic and physiological processes remained constant through time. This could complicate models of the temporal evolution of the Ca isotopic composition of seawater by introducing a variable fractionation factor between seawater and the carbonate sink.

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Seawater calcium isotopes from marine barite: A potential record of carbonate deposition in the oceans

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Carbonate deposition and dissolution significantly affect oceanic alkalinity, atmospheric CO₂ and ultimately Earth's climate. Despite over a century's worth of research on various aspects of the carbonate system, we are just beginning to understand the complexity of the system and elucidate the feedbacks among the processes that control it. The biological precipitation of calcium carbonate largely controls the calcium (Ca) isotope ratio in seawater as a result of the discrimination against heavy isotopes associated with this process. This isotopic fractionation causes seawater to be enriched in the heavier isotopes of Ca relative to its input sources to the ocean, primarily terrigenous and hydrothermal. Reconstructing the seawater Ca isotope ratio over time could be used to quantify the fluctuations in the amount of calcium carbonate deposited in the oceans at any given time assuming some knowledge of the isotopic composition of the sources and sinks.

Previously published paleo-seawater Ca isotopic records used bulk marine carbonates, select species of foraminifera, and phosphorites as their source for reconstruction of seawater Ca isotopic composition. However, multiple factors (temperature, precipitation rate, species-specific vital effects and diagenetic alteration) affect the Ca isotope ratio in each of these phases and its preservation of the seawater signal, thus results are complicated to interpret.

We present Ca isotope data from marine barite, a phase extracted from marine sediments. Barite forms inorganically in the water column and is not directly associated with specific organisms. Assuming that marine barite forms in isotopic equilibrium with contemporaneous seawater and that Ca is incorporated into its crystal structure, it should record the fluctuations in the $\delta^{44}\text{Ca}$ of seawater. Preliminary results from coretop samples indicate marine barite does form in isotopic equilibrium with contemporaneous seawater with an equilibrium fractionation factor larger than that interpreted from precipitation experiments for inorganic calcite. When used in conjunction with other phases, marine barite may eliminate complications inherent in previously published data and result in a more coherent paleo-seawater curve.

Zinc isotope variations in phytoplankton and seawater

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The distribution of Zn in the ocean is largely controlled by biological uptake and remineralization, being drawn down from several nanomolar concentrations in the deep ocean to picomolar concentrations in the surface ocean. Zn isotopes may record this biological activity based on the preferential uptake of lighter Zn isotopes by phytoplankton. We have investigated the Zn isotope composition of modern seawater and plankton tows (Fig. 1), and studied Zn isotope fractionation by phytoplankton in culture, to gain a better understanding of how Zn isotopes may be used to trace biological processes in both the modern and ancient oceans.

Sample type/location	$\delta^{66}\text{Zn}$ (‰)
Seawater	
Northwest Pacific	+0.46
Plankton Tows	
Western S. Atlantic	+0.17 to +0.32
Central N. Pacific	+0.44
Northwest Pacific	-0.22 to -0.02
Bering Sea	-0.08 to +0.00
Alaskan Shelf	-0.44 to -0.39

Figure 1: The isotopic compositions of natural seawater and plankton tows.

Isotope measurements were made on an IsoProbe multicollector ICP-MS, with analytical precision between 0.02 and 0.04‰. Seawater was collected from the Northwest Pacific and Zn was extracted by co-precipitation with Mg(OH)₂. Our measured value is similar to values measured for continental materials. In-situ plankton were collected by trace metal clean plankton tows from both the Atlantic and Pacific Oceans. Our samples show a range of nearly one permil between the heaviest and lightest plankton tows, which we interpret as evidence of fractionation during biological uptake. The diatom *T. pseudonana* grown in culture was also observed to fractionate Zn, preferentially taking up lighter Zn isotopes with an $\epsilon = +0.2$ to $+0.4$ ‰.

Additional seawater and plankton tow samples are being measured in order to better understand the distribution of Zn isotopes in the oceans. Additional species of marine phytoplankton are being studied to compare the isotope effects associated with biological uptake.

Iron isotopes in the marine system

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Iron is an essential micronutrient and is proposed to play a role in climate change by influencing primary production in the ocean. Although the importance of Fe in the ocean has been recognized for the past decade, it is difficult to study because of its complex chemistry and behavior. Fractionation of Fe isotopes could be an effective tool to investigate and quantify the marine geochemistry of Fe. Initial studies of stable Fe isotopes show measurable fractionation in both natural samples and laboratory studies spanning 4‰ (in the 56/54 ratio, $\delta^{56}\text{Fe}$). However, most natural samples measured are in the solid phase (high Fe) with only a few studies of natural aqueous or biological samples (typically lower concentrations of Fe). This study addresses questions about the modern Fe cycle using direct measurements of stable Fe isotopes in a variety of natural samples including trace metal clean plankton tows, river samples, aerosol leachates, marine sediment trap samples, and marine porewaters. Fe isotopic composition was measured on a GV Instruments IsoProbe Multi-collector ICPMS. External precision for the $\delta^{56}\text{Fe}$ measurement is typically better than $\pm 0.2\text{‰}$ (2σ) for natural low-level Fe samples using sample-standard bracketing.

The $\delta^{56}\text{Fe}$ of the marine samples varied by over 4‰ with plankton tows showing a large range (-3.87‰ to +0.36‰). The range in the $\delta^{56}\text{Fe}$ of the plankton tow samples demonstrates that significant and potentially useful fractionation is associated with cycling of Fe in the upper ocean. The Fe in the plankton tow samples in this study was a mixture of intracellular and extracellular Fe. For plankton samples with Fe:C ratios greater than 70 $\mu\text{mol/mol}$, the $\delta^{56}\text{Fe}$ values were more variable and became isotopically heavier with increasing Fe:C ratios suggesting that extracellular Fe is isotopically heavier than the intracellular Fe. Plankton samples from the Atlantic scatter around a hypothetical mixing line between a planktonic intracellular $\delta^{56}\text{Fe}$ of approximately -1.5‰ and an extracellular component of Fe that is isotopically similar to igneous rocks (0‰). The North Pacific plankton tow samples were isotopically lighter in $\delta^{56}\text{Fe}$ than the Atlantic plankton samples.

Boron isotope variation and its environmental implication in Wuquan River Estuary, Hainan Island, China

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The boron-isotope composition of authigenic carbonate skeletons may provide a useful tool to record secular boron-isotope variations in seawater at various times in the geological record. The potential use of boron-isotope geochemistry in skeletons can be as a tracer for palaeoenvironments (Vengosh *et al.*, 1991). Gastropoda skeletons for this study were isolated from Core K4 collected in Samei Lagoon located in Wuquan River Estuary, Hainan Island, China. Their isotopic compositions of boron were measured by TMIS with the method of negative thermal ionization producing BO_2^- ions. The results are shown in the table below.

Sample Depth (cm)	Group	$\delta^{11}\text{B}$ (‰)
14-15	Gastropoda	6.3
34-35	Gastropoda	10.0
125-126	Gastropoda	10.4

$\delta^{11}\text{B}$ values of Gastropoda skeletons range from 6.3-10.4‰. Below the depth of 34-35 cm in the core, the values are about 10‰, which are similar to those in modern marine biogenic carbonates (13.3-32.2‰) (Barth, 1993). In the depth of 14-15 cm (about 1900 AD, Ge *et al.*, 2003), the value is relatively lower (6.3‰), which may reflect a more "terrestrial" boron-isotope signature of the water (Vengosh *et al.*, 1991). $\delta^{11}\text{B}$ record implicates that Samei Lagoon was formerly an embayment and since 1900, the water salinity has become much lower, which is consistent with those of organic carbon isotope values and C/S ratios (Ge *et al.*, 2003).

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Sulfur multiple isotope constraints on the Cenozoic-Cretaceous sulfur cycle

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Marine barite provides a robust record of the isotopic evolution of seawater sulfate (Paytan et al., 1998, 2004). We are extending the existing data set of $\delta^{34}\text{S}$ values with high-precision sulfur multiple isotope measurements of marine barite from the last ~120 Ma. Measurements of ^{33}S and ^{36}S abundances provide information that is complementary to ^{34}S abundances for two reasons, both of which require high-precision measurements to be meaningfully applied. First, individual processes can fractionate sulfur multiple isotopes along trajectories other than the reference mass-dependent fractionation lines that are defined by

$$\Delta^{33}\text{S} = \ln(\delta^{33}\text{S}/1000+1) - 0.515 \times \ln(\delta^{34}\text{S}/1000+1) = 0,$$

and

$$\Delta^{36}\text{S} = \ln(\delta^{36}\text{S}/1000+1) - 1.9 \times \ln(\delta^{34}\text{S}/1000+1) = 0.$$

Second, the trace abundance approximation is valid for the sulfur multiple isotope system, which results in linear isotope mass-balance equations. Isotope fractionation follows an exponential relationship, however, and the co-operation of fractionation and mass balance can produce nonzero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. Recent calibrations of sulfur multiple isotope effects due to different bacterial metabolisms (e.g., Johnston et al., 2005) allow for a rigorous interpretation of the sulfur multiple isotope evolution of seawater sulfate. We use these calibrations in simple isotope mass-balance models to constrain relative mass fluxes through different sulfur conversion pathways. External reproducibility in sulfur multiple isotope measurements are <0.01‰ for $\Delta^{33}\text{S}$ and <0.1‰ for $\Delta^{36}\text{S}$. At their present range of variability (e.g., $\Delta^{33}\text{S}_{\text{max}} - \Delta^{33}\text{S}_{\text{min}} \sim 0.08$; $\Delta^{36}\text{S}_{\text{max}} - \Delta^{36}\text{S}_{\text{min}} \sim 1.0$), our measurements are producing an information-rich record ($\Delta^{33}\text{S}$ signal/noise > 8, $\Delta^{36}\text{S}$ signal/noise > 10) of the Cenozoic-Cretaceous sulfur cycle.

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Using the multiple isotopes of sulfur to constrain microbial processes in the Proterozoic ocean

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It has been argued that widespread sulfidic deep ocean conditions during the Proterozoic resulted from a predominance of sulfate reducing bacteria (SRB) and their effects on the biogeochemical sulphur cycle [1]. It has further been suggested that sulfur disproportionation (SDB) metabolisms did not begin to play a significant role in the cycling of sulfur until early in the Neoproterozoic [1]. Differences in the metabolic style of SRB and SDB cause measurable differences in the $\Delta^{33}\text{S}_{\text{sulfate}}$ that can be used to evaluate these hypotheses [2, 3].

Here we present measurements of the four stable isotopes of sulfur (^{32}S , ^{33}S , ^{34}S , ^{36}S) for proxies of seawater sulfate (CAS, evaporite sulfate, and barite) that we use to evaluate these hypotheses and to test our earlier proposals. Reproducibility of these measurements are 0.01 ‰ or better, clearly demonstrating a small negative excursion of $\Delta^{33}\text{S}_{\text{sulfate}}$ from samples older than ~1 Ga and a small positive excursion for $\Delta^{33}\text{S}_{\text{sulfate}}$ from samples younger than ~1 Ga (Fig 1).

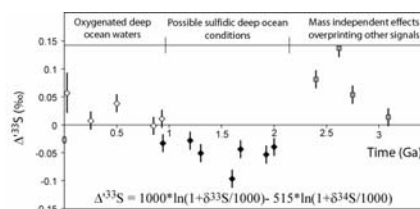


Figure 1: $\Delta^{33}\text{S}$ of oceanic sulfate proxies versus time.

We interpret negative $\Delta^{33}\text{S}_{\text{sulfate}}$ to imply a SRB dominated biogeochemical sulfur cycle while small positive $\Delta^{33}\text{S}_{\text{sulfate}}$ may reflect the added influence of SDB, both have implications for the oxidation state of the Proterozoic ocean.

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Dynamic ocean chemistry around the Marinoan glaciation – Isotopic evidence from cap carbonates

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Hurtgen et al. (2002) suggested that the oceanic sulfate pool would become strongly enriched in ³⁴S during the Neoproterozoic snowball Earth due to continuous bacterial sulfate reduction and lack of supply of S from continental weathering. Overturn of this deep ocean with high $\delta^{34}\text{S}_{\text{sulfate}}$ would have caused a large positive excursion in the $\delta^{34}\text{S}$ of CAS (carbonate-associated sulfate) in cap carbonates.

Comparable large positive excursions in $\delta^{34}\text{S}_{\text{sulfate}}$, more than 25‰, occur in the Doushantuo cap carbonates following the Marinoan glaciation as shallow-water platform facies on the Yangtze Block. Yet, $\delta^{34}\text{S}$ for CAS from the deep-water cap carbonates of the Jinjiadong Formation do not support the Hurtgen et al. (2002) model. Significantly different from the Doushantuo Formation, CAS from carbonate of the Jinjiadong section has lower $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values: 11.2 to 19.7‰ with an average of 14.9 ‰ for S and 5.0 to 8.0‰ with an average 6.6‰ for O, whereas the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values from the Doushantuo cap carbonates fall mostly between 25 to 45‰ and 12 to 18‰ respectively. In the Jinjiadong cap carbonates, the $\delta^{34}\text{S}$ values for pyrite range from 6.1 to 22.9‰ with an average of 14.8‰.

Comparable $\delta^{34}\text{S}$ values for CAS and pyrite suggest two possibilities: 1) the pyrite was formed through bacterial sulfate reduction but at very low sulfate concentration; or/and 2) the sulfate originated from reoxidation of bacterially derived H₂S. A negative correlation between carbonate $\delta^{13}\text{C}$ and CAS $\delta^{34}\text{S}$ supports that BSR probably happened in a stagnant ocean. However, the relatively uniform S and O isotope data for CAS imply that the deep-water, representing coeval ocean water, may have had of $\delta^{34}\text{S}$ values at 15‰ and $\delta^{18}\text{O}$ values around 7‰, rather than the high $\delta^{34}\text{S}$ values described by Hurtgen et al. (2002). Therefore, a dynamic model is proposed to interpret short-term variations in S, C, and O isotopes of global ocean water following the Marinoan glaciation.

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Iron isotope constraints on the Archean and Paleoproterozoic ocean redox state

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The response of the ocean redox state to the rise of atmospheric oxygen by ca. 2.3 Ga ago is poorly constrained although deposition of BIFs until ca. 1.8 Ga suggests at least episodic deep ocean anoxia during the Paleoproterozoic. Since Fe, along with C and S, are coupled with and maintain the redox state of the surface environment, Fe seawater concentration and isotopic composition were likely affected by the change in the redox state of the atmosphere. We will present a study of Fe isotope composition of sedimentary sulfides over geological time and provide evidence for a change in the ocean Fe cycle at the same time as atmospheric redox state changed.

We analyzed Fe isotope compositions of ~ 150 pyrites from 20 black shale units, specifically focusing on Late Archean to Paleoproterozoic time. $\delta^{56}\text{Fe}$ values of handpicked sulfides were obtained using a Neptune MC-ICPMS at WHOI and are reported relative to IRMM-14 with an external precision of 0.1‰ at 2 σ level.

The emerged general pattern of Fe isotope record allows dividing the Earth's history into three stages which are strikingly similar to the stages defined by the $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ as well as other indicators of the redox state of the atmosphere and ocean. (1) Stage 1 (>2.8 to 2.3 Ga) is characterized by highly variable and negative $\delta^{56}\text{Fe}$ values of pyrite (down to -3.5‰) that are interpreted to reflect the reservoir effects during partial oxidation of hydrothermally-derived Fe(II) and precipitation of Fe-oxides. (2) Stage 2 (2.3 to ~1.6 Ga) is characterized by $\delta^{56}\text{Fe}$ values ranging from -0.3 to 1.2‰ that might be related to the increased effect of sulfide precipitation in a redox-stratified ocean. (3) Stage 3, from 1.6 Ga through the Phanerozoic, is characterized by sedimentary pyrite having a limited range of $\delta^{56}\text{Fe}$ variations (less than 0.5‰ around igneous value at ~0‰) reflecting the establishment of an Fe-poor oxygenated ocean.

Ion microprobe carbon isotope analysis of Archean microfossils?

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Metapelites of the Archean Wutai Group (>2.5 Ga) of North China have been found to contain abundant graphite discs. These discs are confirmed to be composed of carbon by elemental mapping through electron and Raman microprobe analyses. Application of the graphite Raman geothermometer suggests these discs experienced metamorphic temperatures of ca. 500°C, consistent with the amphibolite grade of the host rock. We investigated these circular discs by ion microprobe techniques to determine whether they are metamorphic or biological in origin. It has been suggested that these simple discs, which are 20-220 µm in diameter, were originally spherical vesicles of acritarchs (potentially eukaryotic photoautotrophs) with a thick resistant organic wall, and that these were deflated and compressed during compaction and diagenesis. Some of the discs show evidence of folding, breakage, and medial split, all of which are seen in younger acritarchs with coherent and robust walls. If correct, the discovery of these acritarchs would extend the range of eukaryotic fossils back into the Archean, consistent with recent biomarker data. Ion microprobe analyses of five different discs were conducted with the Cameca 6f ion microprobe at high mass resolution at the Carnegie Institution of Washington. The magnitude of instrumental mass fractionation (IMF) inherent to surface ionization mass spectrometry was quantified by the repeated (n = 7) analysis of the standard Mao diamond ($\delta^{13}\text{C} = -6.5\%$, IMF = $53.1 \pm 0.4\%$). The primary Cs⁺ beam intensity was 0.5 nA and was focused down to a 20-25 µm spot, which allowed for multiple analyses of the same individual. In most cases the variability of $\delta^{13}\text{C}$ values between spots on the same individual was small (< 2%), but the range of values between different individuals spanned from -7.3 to -35.8%. The overall average of all analyses is close to the -21.3‰ value determined by standard techniques for bulk kerogen. The wide variability between individuals may be tentatively interpreted as biological in origin, insofar as metamorphic graphite measured by the same ion microprobe technique shows much smaller magnitude of variation in primary grains lacking secondary overgrowths.

Molybdenum isotope prospects

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The oxygenation of the oceans has varied through time but the timing and extent of these variations are not well understood, nor do we have a good understanding of the connections between changes in atmospheric and ocean oxygenation. The development and refinement of ocean paleoredox proxies is therefore a high priority.

The molybdenum (Mo) stable isotope system is emerging as a valuable tool for investigating ocean paleoredox. To first order, Mo enters the oceans via rivers and is removed in oxic environments by adsorption to Mn oxides and in sulfidic settings via scavenging of Mo oxythiomolybdates. The isotopic contrast between these sinks is ~ 2 ‰. Hence, the steady-state Mo isotope composition of the oceans should reflect the balance between Mo removal to Mn-oxides vs. removal in sulfidic settings. Fractionation occurs during removal to Mn-oxides. Today, this process generates a steady-state isotopic offset between average crustal Mo (~0‰) and seawater (~ 1.6‰). This offset would have been smaller - i.e., seawater isotopically lighter - during extended periods of expanded ocean anoxia because a smaller fraction of isotopically light Mo would have been buried in association with Mn-oxide sediments. This system is particularly valuable because it may constrain regional or global ocean redox, rather than only local redox, as a result of the long ocean residence time of this element.

Mo isotope systematics are already being used to obtain qualitative and semi-quantitative information about ancient ocean redox (e.g., Arnold et al, 2004). Quantitative applications require better understanding of a number of parameters, including: The importance of suboxic ($\text{O}_2 < 5 \mu\text{M}$) settings for Mo removal and isotope fractionation; the magnitude of isotope fractionation during adsorption to Mn oxides and the sensitivity of this fractionation to temperature and other variables; and Mo isotope variability due to weathering and riverine transport. The current status of research in these areas will be reviewed.

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Effect of rice growth on geochemical circle of silicon: Silicon isotope study on rice plants grew in field and laboratory

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Geochemical circle of silicon attracts more attention recently and plants play important role in global silicon geochemical circle. To understand the effect of rice growth on silicon geochemical circle, a silicon isotope study was carried out on rice plants grew in field and laboratory. It is found that the silicon contents increase from roots to stem to leaves, and then decrease to husks and grains (Fig. 1). It is also found that the silicon content in rice growth water solution reduces from 20ppm to around 1ppm in 4-5 days.

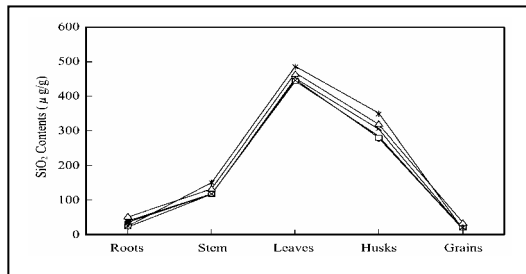


Fig.1 Variation of SiO₂ contents in various rice organs

The $\delta^{30}\text{Si}$ values decrease from roots to stem, but increase from stem through leaves to husks and rice grains. When the silicon contents in water decrease from 20ppm to around 1ppm, the $\delta^{30}\text{Si}$ value increases 2-3‰. These facts can be explained with two kinetic isotope fractionations: one occur when silicon is taken by roots and the other occur when silica precipitate in plants. Based on these results, the effect of rice growth on silicon geochemical circle is discussed.

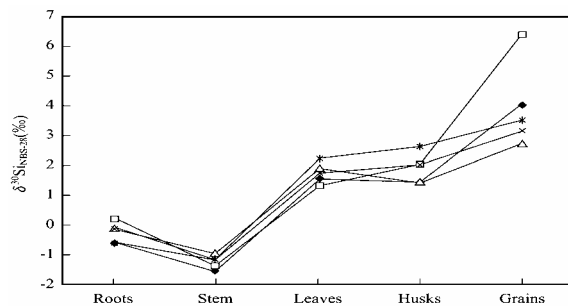


Fig.2 Variation of $\delta^{30}\text{Si}$ values of various rice organs

The life history and stock structure of groundfish from stable isotopic analysis of otoliths

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The study of stable oxygen and carbon isotope ratios of otoliths ($^{18}\text{O}/^{16}\text{O}$ or $\delta^{18}\text{O}$, and $^{13}\text{C}/^{12}\text{C}$ or $\delta^{13}\text{C}$) has yielded valuable information on the life history and behaviour of some commercially important fish species along the Pacific west coast, particularly in identification of spawning aggregations and stock structure. Here we present a comparison study from otoliths of Pacific cod (*Gadus macrocephalus*), sablefish (*Anoplopoma fimbria*), and yelloweye rockfish (*Sebastes ruberrimus*). In general, the $\delta^{18}\text{O}$ values of Pacific groundfish started with a low range from -0.5 to 0.5‰ VPDB, and then increased to +1.8 ~ 2.5‰ VPDB as the fish get sexual maturity. The initial low isotopic values correspond to the natal sources, while the stable higher isotopic values correspond to the adult stage before the fish were caught. Similar isotopic variations were found in $\delta^{13}\text{C}$ from -5.0 to -2.5‰ VPDB at the breeding stock and from -0.5 to 0.5‰ VPDB as adults. The stable $\delta^{18}\text{O}$ values at the adult stage indicate that these groundfish might live at similar oceanic conditions, whereas their different $\delta^{13}\text{C}$ values in the juvenile stage reveal that the fish might have different diet or food sources. Based on isotopic records, we recognized two or more separate spawning stocks or subpopulations for Pacific cod and sablefish, except for yelloweye rockfish. It seems that the difference might relate to the different life history and behaviour, and stable isotopic signatures in otoliths could be used as a natural tag for identification of marine fish stocks. Thus, a new project on the stock structure of Pacific sardine (*Sardinops sagax*) has been initiated and the otolith analysis is underway.

High mass resolution plasma mass spectrometry of Cr isotopes

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Natural mass dependent isotope fractionation of Cr is linked to changes in its oxidation state, and is a promising tracer for secular variations in the reductive capacity of the oceans. The expected isotope variations of a few permil in nature require high precision measurements. We developed a double spike technique, with high mass resolution that renders molecular interferences (e. g., from ArN) negligible at relatively small ion beams of $4\text{--}5 \times 10^{-11}$ A for ⁵²Cr. The double spike approach for correcting instrumental mass bias was compared with the standard-bracketing technique by using aliquots of a double spiked Cr standard. Reproducibility of the double spike-corrected ⁵³Cr/⁵²Cr ratios was 20 ppm (2σ), similar to internal isotope normalization of unspiked samples for TIMS. The most precise data were obtained by combining double spike and standard bracketing of data obtained in a measurement sequence. The instrumental mass bias was corrected using the double spike, and the δ-values were constructed as deviations from the mean value of the standards measured in the sequence. This approach yielded 10 ppm precision (2σ) for δ⁵³Cr, which is twice as good as the double spiked ⁵³Cr/⁵²Cr ratios by themselves, or for δ-values constructed with an assumed constant value of the normalizing ⁵³Cr/⁵²Cr ratio. Eliminating the instrumental mass bias through standard bracketing yielded an overall uncertainty of ~100 ppm, reflecting drift in the instrumental mass bias during the duty cycle (not optimized for this experiment). The double spike measurements are unaffected by changes in mass bias drift, which in practice is dominated by subtle differences in the levels of matrix ions between samples and standards.

Fe isotope composition in Neoproterozoic dolomite rocks and banded iron formations

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The Neoproterozoic geological record provides evidence of some of the most extreme environmental changes in Earth history; however, the cause(s) behind these changes remain controversial. Here we present a novel Fe-isotope dataset from Neoproterozoic dolomitic rocks and banded iron formations (BIFs) from the Otavi Group, southern Congo Craton, NW Namibia. Samples bracket two distinct glacial intervals, the lower Chuos Fm. and the upper Ghaub Fm. [1]. Fe-isotope compositions were measured relative to IRMM-014 and determined by high-resolution, multiple collector, ICP-MS with an external precision (1 σ) on δ⁵⁶Fe of ± 0.05 ‰. The initial 65 m of cap dolomite deposited after the lower Chuos glacial is characterised by negative ⁵⁶Fe composition of - 0.45 ‰. The overlying deposits show an increase in δ⁵⁶Fe values of -0.1 to 0.1 ‰, consistent with pre-glacial compositions. BIFs deposited throughout the Chuos glacial interval have an average δ⁵⁶Fe composition of - 0.03 ‰. The pre- and postglacial successions around the upper Ghaub glacial interval show consistent δ⁵⁶Fe values of c. - 0.27 ‰. Notably, the postglacial cap dolomite exhibits a negative δ¹³C excursion up to - 4.5 ‰ [2]. Significant Fe-isotope excursions have been predicted to occur in oceans during major glacial events because of changes in sources of Fe fluxes entering the oceans [3]. The lack of significant changes in Fe-isotope composition in the upper Ghaub cap dolomite, where a negative δ¹³C excursion occurs, implies that either a major change in Fe-source fluxes did not occur or that the signal has not been preserved, thus necessitating a better understanding of fluid-mineral fractionations in the Fe-dolomite system.

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Re-Os isotopes as a tracer and dating technique for black shales and ocean anoxic events

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Oceanic anoxic events took place many times in the Earth history, which usually produced large amounts of black shale deposition. The study on genesis and exact age of these oceanic anoxic events has become one of the frontier research areas in palaeoceanography. The study of oceanic anoxic events can help us to better understand palaeo-ocean environment change, earth system evolution, effect of other Earth-spheres to biosphere, as well as ore genesis and oil formation and its environment. Hence, in recent years the study of oceanic anoxic events has focused on many aspects such as palaeoceanography, palaeo-climatology, palaeo-geography, palaeotology, tectonic, geology and geochemistry. Among these studies, exact dating of the oceanic anoxic events is one of the key tasks, and if the applied isotope system can, at the same time, provide information on palaeo-ocean environmental change, it will enhance our understanding on the genesis of the oceanic anoxic events. Re-Os isotope system is such a recently developed new geochemical technique, which can serve these purposes perfectly. The organic-rich black shales are most suitable for Re-Os isotope dating, and can produce very precise geological age. Furthermore, using Os isotope data of marine sediments, we can obtain information on paleo-seawater Os isotopic compositions and their evolution during geological time. In South China, multi-periods of oceanic anoxic events occurred from Neoproterozoic to Cambrian, and huge thickness of black shales precipitated. Therefore, using Re-Os isotope method, not only we can determine the time of such events, but also paleo-oceanic environment can be traced effectively.

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