

## A calculational procedure for determining $^{17}\text{O}/^{16}\text{O}$ ratio in water by an equilibration method

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Stable isotope ratios of water ( $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$ ) are useful for studies of the modern and past hydrologic cycle. In addition,  $^{17}\text{O}/^{16}\text{O}$  ratio in water provides a parameter which reflects relative humidity changes above the ocean,  $^{17}\text{O}$ -excess [1]. However, the  $\delta^{17}\text{O}$  data of water are very limited due to the technical difficulties of precise measurement involving fluorination reaction to convert water to gaseous  $\text{O}_2$ . Recent study showed that the equilibration method can be used for  $\delta^{17}\text{O}$  measurement, and proposed to use a chemical buffer in the water to keep the pH value [2].

We have developed a relatively simple calculation scheme for retrieving the  $\delta^{17}\text{O}$  of water from the 45/44  $\text{CO}_2$  ion-abundance data ( $^{45}\text{R}$ ) obtained by the conventional equilibration method. Our calculation takes into account a decrease in pH value due to high partial pressure of  $\text{CO}_2$  during the equilibration process. Further, we rephrase the equations in terms of  $\delta$  value. This reveals that the  $\delta^{17}\text{O}$  of water can be determined precisely when the relative  $\delta^{13}\text{C}$  differences between working standards and sample are negligible.

Application of the calculation scheme to the IAEA standard waters show the  $\delta^{17}\text{O}$  of GISP is consistent with that of previous studies. We also have applied this method to the deep ice core drilled at the Dome Fuji station, Antarctica. A 130m section around MIS9.3 (~ 330kyr BP) was measured with continuous 10-cm sampling. The profile of  $\delta^{17}\text{O}$  shows a marked similarity to that of  $\delta^{18}\text{O}$ . The changes in  $^{17}\text{O}$ -excess during the glacial-interglacial shift can be detected by averaging many data points.

[1] Barkan & Luz (2007) *Rapid Communications in Mass Spectrometry* **21**, 2999-3005. [2] Elsig & Leuenberger (2008) *Analytical Chemistry* **80**, 3244-3253.

## Carbonyl sulfide (OCS) in the Archean atmosphere

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The mass independent fractionation of sulfur isotopes (S-MIF) in geological samples would provide a record of the past atmospheric composition, though the mechanism of photochemical S-MIF is still poorly understood [1]. We determined the high-precision UV absorption spectra of  $\text{SO}_2$  isotopologues [2] and calculated isotope fractionation factor of  $\text{SO}_2$  photolysis as a function of wavelength. Using these results, we show that the estimated fractionation factors give mass independent distributions and are highly sensitive to the atmospheric concentrations of  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CS}_2$ ,  $\text{NH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{S}$ , OCS and  $\text{SO}_2$  itself, because these molecules can modify spectra of actinic UV flux. Although various UV-shielding scenarios can be considered, we found that the negative  $\Delta^{33}\text{S}$  observed in all the Archean sulfate deposits [1,3] could be expected only when OCS was present in the atmosphere. This is because OCS uniquely absorbs >200 nm region of solar UV flux. Further, we performed numerical simulation of atmospheric reactions including OCS chemistry and found that ppm-level OCS could be accumulated in a  $\text{O}_2$ -free reducing atmosphere when  $\text{CO}/\text{CO}_2$  ratio is greater than 1. Therefore, appreciable amount of OCS is likely to have existed in the reducing Archean atmosphere. Such a high level of OCS also absorbs infrared light from 8 to 13  $\mu\text{m}$ , which is not absorbed by water vapor. Hence, OCS could be an alternative or even more efficient greenhouse gas than  $\text{CO}_2$  to resolve the faint young Sun paradox [4]. Furthermore, OCS also has absorption band in lethal UVC region like ozone, thus could be an alternative UV-shielding molecule in an  $\text{O}_2$ -free reducing atmosphere. The decline of OCS might have caused the late Archean Pongola glaciation (2.9 Ga) and possibly resulted in UV crisis of terrestrial and shallow water ecosystems until the rise of oxygen.

[1] Farquhar *et al.* (2001) *JGR* **106**, 32829. [2] Danielache *et al.* (2008) *JGR* **113**, D17314. [3] Ueno *et al.* (2008) *GCA* **72**, 5675. [4] Sagan & Mullen (1972) *Science* **177**, 52.

## Impact of high CO<sub>2</sub> concentrations on the structure of microbial communities in marine sediments

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Microbial communities represent one of the key levels for ecosystem functioning, but their short- and long- term structural and functional responses to changes in ocean pH are not well understood. Sedimentary hydrothermal vent systems leaking CO<sub>2</sub> provide natural gradients in pH and CO<sub>2</sub> concentrations which can be studied as natural analogues to small pH changes, as caused by ocean acidification, and dramatic pH changes, as by focused CO<sub>2</sub> leakage from subsurface reservoirs. Although most studies focused on planktonic communities, only two previous studies have investigated the effects of increased CO<sub>2</sub> levels on benthic ecosystems (Inagaki et al. 2006; Hall-Spencer 2008). Here we examined how natural gradients in pH and CO<sub>2</sub> flux across the Yonaguni Knoll basin of the Okinawa trough impact benthic bacterial communities. Changes in function were assessed as differences in the sustained biomass, and in the respiration of reduced compounds. Changes in bacterial community structure were analysed by community fingerprinting using ARISA (Automated Ribosomal Intergenic Spacer Analysis). Our data show a strong shift in benthic bacterial community structure and function along in situ pH gradients.

## Degradation of oil via combination reactions under water pressure in geological basins

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Based on modelling the results from numerous pyrolysis experiments, it has been predicted that oils become thermally unstable at temperatures between 150 and 200°C and crack to lighter hydrocarbons (gas) and pyrobitumen. This hypothesis has been derived using the results from mainly dry or anhydrous pyrolysis experiments, with the models based largely on first order kinetics. Pressure has either been considered to have no effect or a significant effect on the rate at which the oil cracks into lighter products and coke. However both thermodynamic and transition state theory indicate that oil cracking should be retarded by water pressure, and we have recently reported reduced cracking to gas during source rock maturation at high water pressures [1].

In experiments at 350°C under part water, part vapour conditions, oils crack to gases and pyrobitumen due to the ease at which the vapour phase can be compressed. However, when heated under water pressure (500 bar), the extent of cracking is reduced and combination reactions are evident. Such combination reactions are exothermic, whereas cracking reactions are endothermic, suggesting that in basins at temperatures greater than which biodegradation can occur, this pathway can provide a new method for generating tars and bitumens from trapped oils. In deep, relatively cool, high-pressure basins such as the Gulf of Mexico, tars and bitumens are sometimes encountered at depth (20,000 ft.+), and under these conditions combination reactions should be highly favoured over cracking reactions.

However, the effect of water pressure appears limited as with pyrolysis at 420°C under water-pressure (450 bar), thermal cracking occurs. However such temperatures are very unusual in geological basins, but if hot volcanic waters flow through shallow reservoirs containing oil, then cracking may be favoured due to the very high temperature-low pressure conditions.

[1] Carr *et al.* (2009) *Pet. Geoscience* **15**, 17-26.

## Stable isotope variations in a modern North Sea oyster shell reflect annual environmental changes

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$\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of low-Mg-calcite fossils have been widely used to reconstruct paleoclimatic and paleoenvironmental conditions [1, 2]. The stable-isotope composition of modern *Crassostrea virginica* shells for example reflects both temperature and salinity variations [3], but these samples originate from an estuarine habitat with considerable annual changes in salinity. In the present study we have focused our attention on  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values from a single specimen of the modern Pacific oyster *C. gigas* from a sub-tidal oyster bank in the List Basin east of Sylt Island (North Sea, Germany) where fully marine conditions occur all the year round. We sampled along a traverse in growth direction through the umbo of the shell and analyzed 181 samples for their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Oxygen-isotope values vary periodically between -2.5 and +1.3 ‰. We interpret these fluctuations, taking the natural seawater  $\delta^{18}\text{O}$  changes into account, to reflect the annual seawater temperature variations of about 20°C that are reported for this region. These occur constantly over the four years of the oyster's life, indicating that shell build-up took place continuously from spring to autumn. These results are in contrast to earlier observations that some bivalves stop shell secretion in the summer months after reaching sexual maturity [4]. The  $\delta^{18}\text{O}$  results further indicate that *C. gigas* grows from approximately March to November, in accordance with biological results [5]. The relatively high variability in oxygen-isotope ratios suggests that minimum temperatures for the onset of growth in *C. gigas* are near 6°C, not near 10°C as hitherto suspected for this and other *Crassostrea* species [6, 7]. The  $\delta^{13}\text{C}$  values of the *C. gigas* shell show that a sudden 1 to 2 ‰ positive excursion to heavier values occurs in the spring secretions of any annual cycle. These trends may be caused by enhanced biological production in the seawater or by metabolic processes of the oyster.

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## Differentiation of hydrous calc-alkaline magmas at mid to lower crustal levels: Experimental constraints

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Formation and growth of juvenile arc crust from primary mantle-derived, hydrous, calc-alkaline magmas is a polybaric process. Compositions of magmas separating from mantle residues are modified through interaction with lithospheric mantle and lower crust and by crystallization-differentiation that drives them towards andesitic to dacitic liquids forming the major part of the middle and upper arc crust.

Here we summarize the results of equilibrium and fractional crystallization experiments targeted at the evolution of primary mantle-derived and derivative hydrous magmas under conditions prevailing at the base and in the lower part of a growing island arc crust (0.8-1.5 GPa). Employed primary picrobasaltic to high-Mg andesite starting materials are representative for mantle extraction depth varying between 90 and 40 km. We investigated the mutual phase relations of the principal phases olivine, cpx, opx, garnet, amphibole, plagioclase and spinel. At pressures exceeding 0.8 GPa (25km) between 45 and 70% of ultramafic, clinopyroxene and amphibole dominated cumulates are produced to obtain andesite to dacite compositions that are typical for more evolved island-arc magmas and rocks (tonalites) forming the upper part of the igneous system. Delayed plagioclase crystallization at the expense of early amphibole saturation shifts derivative liquids closer to the metaluminous / peraluminous limit or even within the peraluminous field with increasing pressure.

Trace element partitioning between the principal higher pressures phenocryst phases (cpx, opx, garnet, amphibole) and basaltic to dacitic liquids along the liquid line of descent has been determined at 0.8-1.5 GPa. We utilized these new partitioning data to model the trace element evolution of liquids experimentally produced by fractional crystallization at 1.0 GPa. We found that computed REE and trace element patterns reveal striking similarity with natural examples from plutonic complexes showing petrological evidence for high-pressure evolution (early amphibole, delayed plagioclase) expressed for example by steep REE patterns and high Sr/Y ratios commonly attributed to slab melt contributions and/or involvement of garnet in their genesis.

## The New Caledonia Ophiolite: Multiple melting stages and refertilisation process as indicators for ridge to subduction formation

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The New Caledonia island is a patchwork of sedimentary, volcanic and ultrabasic units. The ophiolite complex consists in a main body in the south of the island and some isolated klippe located along the NW coast. This terrane thrusts the magmatic Poya terrane, essentially made of undepleted MORB with some BABB, OIB and boninites.

Most of the ophiolite consists of highly depleted harzburgites (+/- dunites) with characteristic U-shape REE patterns whose chemical composition indicates a likely formation in a forearc environment. However, the northernmost lherzolites are characterized by spoon-shape REE patterns whose origin remained unclear.

Our new REE data on whole rock and minerals demonstrate the abyssal affinities of the lherzolites. These peridotites are best explained by partial melting in a ridge environment followed by a refertilisation that led to a significant LREE enrichment of the lherzolites. Using equilibrium melting equations, we find that the liquids extracted from these lherzolites are similar to the undepleted MORBs from the Poya terrane. This suggests that the entire sequence could represent the oceanic lithosphere of the South Loyalty Basin (SLB) formed during the Campanian to the late Eocene. In addition, our study shows that the most depleted harzburgites are best modelled by hydrous melting in a forearc environment of a source that had previously experienced depletion in a ridge environment. The melts associated with this second stage of partial melting are similar to the boninites from the Poya terrane.

The occurrence of two types of melting processes in the same ophiolite most probably reflects the transition from accretion to convergence in the SLB during the Late Paleocene, with the initiation of the subduction at (or near) the ridge axis.

## From Arthur Holmes to Harry Hess: How melting of the mantle controls amagmatic crustal accretion

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Most models of lithospheric generation at slow-spreading ridges favour the theory that melt is focused diapirically toward segment centres, but there is little agreement on focusing mechanisms, or the scales at which they operate.

We examine these mechanisms in detail, both in magmatic spreading areas and 'amagmatic' regions of the Mid-Atlantic Ridge (12°60'N-15°20'N). Here, melt provision is sporadic, and a significant proportion of plate separation is accommodated on low-angle detachment faults, exposing mantle peridotite on the seafloor in oceanic core complexes.

Geochemical analyses of both basalts and peridotites show significant variations along the ridge. Element [8] and trace-element ratios indicate that these variations exist independent of fractionation processes. Pb isotope ratios show a wide variation in initial source compositions over a limited (~15km) geographic extent.

Yb/Lu ratios, taken as a proxy for residual garnet in the melting zone, indicate that amagmatic locations are characterised by high-pressure, low melt fractions. This indicates a short, deep upwelling path (mantle cold spot?) as an explanation for low melt fraction in amagmatic regions. FTIR analysis on basaltic glasses show that mantle hydration also varies along the ridge and that amagmatic positions appear to correlate with 'drier' spots in the mantle.

At amagmatic sites we find that low melt fraction basalts correspond temporally with detachment initiation, whilst zero age basalts at the corresponding position on the axis are derived from typically higher melt fractions.

Our geochemical data indicate that magmatic areas tap volatile-rich mantle and have long upwelling paths, producing high melt fraction basalts that are less enriched in incompatible elements than those from 'amagmatic' sources. In contrast, 'amagmatic' spreading taps drier source mantle over a shorter and deeper upwelling path, producing low melt fraction basalts that are relatively enriched in incompatible elements. We conclude that low melt production at amagmatic regions, resulting directly from mantle compositional characteristics, drives the transition from magmatic to tectonic spreading, and that the low F melts form prior to detachment initiation, but do not necessarily persist during amagmatic spreading.

## $^{142}\text{Nd}$ evidence for an enriched Hadean reservoir in the root of the Bastar craton (India)

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Variations in the  $^{142}\text{Nd}/^{144}\text{Nd}$  composition of terrestrial rocks are a sensitive monitor of major silicate differentiation events on Earth that occurred during the Hadean. For example, the  $^{142}\text{Nd}/^{144}\text{Nd}$  excesses (relative to the La Jolla Nd standard) in some Archaean (3.6-3.8 Ga) rocks from Greenland (e.g., [1–3]) indicate the existence of an early, incompatible element depleted mantle. We have measured  $^{142}\text{Nd}/^{144}\text{Nd}$  deficits (relative to the La Jolla Nd std.) in some Mesoproterozoic (~1.48 Ga) lithospheric mantle-derived alkaline rocks [4] from the Khariar nepheline syenite complex in southeastern India. The  $^{142}\text{Nd}/^{144}\text{Nd}$  isotopic signature of these alkaline rocks thus provides evidence for a reservoir that was relatively enriched in incompatible elements, and formed early in Earth's history (>4.2 Ga). This reservoir—or at least some of its Nd isotope signature—persisted for  $\geq 2.7$  Gyr without being mixed away into the ambient mantle. Its survival may have been facilitated by long-term storage within the lithospheric root of the Bastar craton.

We propose that the  $^{142}\text{Nd}/^{144}\text{Nd}$  deficit observed in these Mesoproterozoic alkaline rocks may be the diluted signature of a relatively enriched, Hadean reservoir. (Whereas the Khariar  $^{142}\text{Nd}$  signatures suggest early enrichment relative to the prevalent terrestrial Nd, i.e., La Jolla, they would still represent an early depletion relative to the chondritic reference.) Interestingly, no  $^{142}\text{Nd}$  evidence of the early depleted mantle has been observed in <3.6 Ga juvenile rocks, possibly implying that such domains had been effectively mixed back into the convecting mantle by that time. Some early, incompatible element enriched components have apparently escaped this fate. Thus, the mantle sampled by magmatism since 3.6 Ga may be biased towards a depleted composition that would be balanced by more enriched reservoirs existing as Hadean crust [5] or as enriched mantle components sequestered within old cratonic roots or perhaps in the D'' layer of the lower mantle.

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## Groundwater nanoparticles in the far-field at the Nevada Test Site

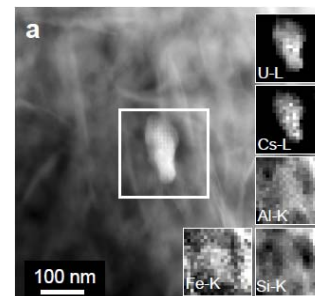
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Colloid-like nanoparticles in groundwater have been shown to facilitate migration of several radionuclides:  $^{239,240}\text{Pu}$ ,  $^{137}\text{Cs}$ ,  $^{152,154,155}\text{Eu}$ , and  $^{60}\text{Co}$  [1]. However, the exact type of nanoparticle and the speciation of the associated radionuclides has remained unknown. We have investigated nanoparticles sampled from the far-field at the Nevada Test Site, Nevada, utilizing advanced electron microscopy techniques, including high-angle annular dark-field scanning TEM (HAADF-STEM). Fissionogenic elements: Cs, rare earth elements (REE), activation elements: Co; and actinides: U and Th, were detected. Cesium is associated with U-forming cesium uranate with a Cs/U atomic ratio of ~0.12 (Fig. 1). Light REEs and Th are associated with phosphates, silicates, or apatite. Cobalt occurs as a metallic aggregate, associated with Cr, Fe, Ni, and  $\pm$  Mo. Uranyl minerals; Na-boltwoodite and oxide hydrates are also present as colloids. Because of these chemical associations with nanoscale particles, in the size range <100 nm, these particles may facilitate transport, and a variety of trace nano-scale phases may be responsible for the migration of fissionogenic and actinide elements in groundwater. In order to accurately model the transport of these contaminants, predictive transport models should include consideration of nanoparticle-facilitated transport.



**Figure 1:** HAADF-STEM of Cs-U-phase with the elemental maps.

[1] Kersting *et al.* (1999) *Nature* **397**, 56-59.

## A thermodynamic and mass transfer analysis of organic/inorganic interactions during thermochemical sulfate reduction in carbonate reservoirs

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Thermochemical sulfate reduction (TSR) occurs in deep carbonate reservoirs at temperatures ranging between 100 and 180°C [1]. TSR involves the reaction of aqueous sulfate with hydrocarbons, which produces hydrogen sulfide (H<sub>2</sub>S), organic sulfur compounds, elemental sulfur, carbon dioxide (CO<sub>2</sub>), pyrobitumen, and other oxidized species of carbon [1, 2]. Water (H<sub>2</sub>O) may be a reactant or product of TSR, depending on the H/C ratio of the reacting hydrocarbon phase.

Although the overall TSR process is irreversible under sedimentary basin conditions, many of the reactions involved in this process appear to proceed at or near equilibrium. For example, gas-phase concentrations of methanethiol (CH<sub>3</sub>SH) in carbonate reservoirs from the Sichuan Basin [3] are consistent with metastable equilibrium involving CO<sub>2</sub> and H<sub>2</sub>S at redox conditions close to the pyrite-pyrrhotite-magnetite buffer. These redox conditions are also consistent with the organic sulfur content of crude oils, which increases with increasing H<sub>2</sub>S content of the gas phase. In contrast, the anhydrite-calcite-sulfur assemblage cannot be stable under these conditions in the presence of an aqueous phase. Accordingly, anhydrite should dissolve irreversibly unless protected by secondary calcite [4].

Based on these observations, mass transfer calculations have been carried out at 150°C and 500 bar to quantify the relative importances of anhydrite dissolution, hydrocarbon destruction, CO<sub>2</sub> and H<sub>2</sub>S generation, petroleum sulfurization, and calcite, sulfur and pyrobitumen precipitation during thermochemical sulfate reduction.

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[4] Bildstein *et al.* (2001) *Chem. Geol.* **176**, 173-189.

## Coexistence of abyssal and ultra-depleted SSZ type mantle peridotites from the Muğla area, SW Turkey

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Mantle peridotites of the Muğla area, south-western Turkey are classified as cpx-harzburgite, depleted harzburgite, and dunite, on the basis of their modal mineralogy, geochemical features, and mineral chemistry. Cpx-harzburgites are characterized by their higher average CaO (2.27 wt.%;  $\sigma = 0.22$ ), Al<sub>2</sub>O<sub>3</sub> (2.07 wt.%;  $\sigma = 0.18$ ), REE (53 ppb;  $\sigma = 13.3$ ), and initial Os isotopic composition (0.12715;  $\sigma = 0.0021$ ), and contain Al-rich pyroxene with lower Cr content of coexisting spinel (Cr# = 17.7;  $\sigma = 1.98$ ). In contrast, depleted harzburgites and dunites are represented with their lower average CaO (0.58 wt.%;  $\sigma = 0.29$ ), Al<sub>2</sub>O<sub>3</sub> (0.42 wt.%;  $\sigma = 0.20$ ), REE (1.24 ppb;  $\sigma = 2.9$ ), and initial Os isotopic composition (0.12113;  $\sigma = 0.0072$ ), and contain Al-poor pyroxene with higher Cr content of coexisting spinel (Cr# = 57.4;  $\sigma = 6.50$ ). Mineral chemistries and whole-rock geochemistry indicate that the depleted harzburgites and dunites experienced higher degree partial melting than those of cpx-harzburgite, which is consistent to be the residua of extraction of MORB type melt (5-15% partial melting) during the sea-floor spreading. Calculated low temperature of equilibration, positive correlation between the Cr# of spinel and oxygen fugacity values, and LREE enrichment against their ultra-depleted nature of harzburgites and dunites, support the idea that cpx-harzburgites have subsequently been modified in a suprasubduction environment by percolation with boninitic melt, produced from high degree partial melting (up to ~35%) of already depleted cpx-harzburgite. Dunites around the chromite deposits are considered to be the product of melt-peridotite interaction.