

Origin of Enstatite Chondrites and Implications for the Inner Planets

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Over 90% of EC chondrules are enstatite-rich. Some enstatite was initially Fs_5 to Fs_{30} , and was reduced after formation, probably by interaction with a vapor in which reduced matrix phases were thermodynamically stable (Lusby *et al.* 1987; Weisberg *et al.* 1994). We are interested in the nature and nebular location of such a reducing vapor, in which EC minerals (e.g.- CaS, MgS) might have been stable.

Ebel and Grossman (2000) mapped dust enrichment conditions for thermodynamic stability of FeO-rich silicates using a CI chondrite dust composition. The highly unequilibrated, anhydrous, interstellar organic- and presolar silicate-bearing cluster IDPs (C-IDPs) may be closer to the primordial dust composition than CI dust, as suggested by observed C depletions, relative to solar, in dense interstellar clouds. C-IDPs are relatively reduced, with low FeO and high C contents. Alexander (2002) noted modest enrichments of C-IDP-like dust would create conditions reducing enough to stabilize EC minerals, unless ice was also concentrated. Also, recent solar photosphere measurements suggest a 25% lower O abundance than previous estimates (Prieto *et al.* 2001).

We calculated condensation using a C-IDP-like dust composition at dust enrichments of 10, 100 and 1000 times solar at $P^{\text{tot}}=10^{-3}$ bar. Oxygen is calculated from a 75% solar baseline. The dust is H-, N-free CI, with all S as FeS, and O sufficient to make rock-forming oxides of the remaining Fe, Si, Mg, etc. At 100x enrichment, CaS is stable below 1290K, and MgS below 1180K. At 1290K, modal pyroxene (Fs_0) and olivine (Fa_0) are approximately equal. Although the system tracks $f(\text{O}_2)\sim(\text{IW}-4)$ above 1720K, $f(\text{O}_2)$ drops to (IW-8) by 1290K. Surprising! Silicate FeO decreases with decreasing T.

These results suggest that at the time the asteroids were forming, the snow line was near the inner edge of the asteroid belt, the presumed location of EC parent bodies. Bodies forming inward of the snow line would have been reduced, unless during high-T processing the dust enrichments relative to gas were modest. This has implications for the terrestrial planets' inventories of highly and moderately volatile element (and water) sensitive to reducing *versus* oxidizing conditions.

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REE, Th and U abundances in individual chondrules from Dhajala, Allegan and Bjurböle chondrites

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It is apparent that chondrules once experienced melting processes of the precursor material. As relict minerals are still present in chondrules of some UOCs, these chondrules may provide us information concerning the precursor materials and melting episodes. Chondrules in EOCs have experienced thermal metamorphism on their parent bodies and, hence, may help us to understand their metamorphic activities. In this study, we separated chondrules from Dhajala (H3.8), Allegan (H5) and Bjurböle (LL4) and studied them for trace element compositions and mineralogical/petrological characteristics.

Chondrules were separated mechanically, embedded in acetone-soluble resin and sawed into three portions. One portion was used for determining REE, Th and U by ICP-MS. Another portion was used for mineralogical and petrological descriptions by SEM and EPMA.

REE, Th and U abundances in Dhajala chondrules are generally unfractionated from and higher than those in the bulk sample. Eu anomaly (negative) is commonly but not ubiquitously observed. There seems no apparent correlation between REE abundances and mineral/petrological characteristics. In contrast, REE, Th and U abundances are largely variable in chondrules of Allegan and Bjurböle even though chondrule types are identical. Lanthanoids (REE) (with positive Eu anomaly) and actinoids (Th and U) are generally fractionated, with REE being relatively depleted. Our study suggests that REE, Th and U abundances in chondrules inherited those from the precursor material. During thermal metamorphism on ordinary chondrite parent bodies, REE migrated into surrounding minerals much faster than Th and U.

Halogen-derived noble gases in the Allende meteorite: A laser microprobe study

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Introduction

Micro-distribution of halogens in meteorites still remains unsolved due to the difficulty of their *in situ* microanalysis. We intend to make the matter clear with noble gas isotopes produced by decay of extinct nuclide ¹²⁹I and by neutron capture on ³⁵Cl, ³⁷Cl, ⁷⁹Br, ⁸¹Br and ¹²⁷I in space. A high sensitive mass spectrometer with a laser microprobe allows us to determine the small quantities of halogen-derived noble gases. In addition, it is convenient that we can investigate only the intrinsic halogens of meteorites independent of terrestrial contamination.

In this study, we investigated micro-distribution of noble gases in the Allende meteorite, mainly a CAI. 7-10 micrograms of meteorite material was melted with laser heating and the extracted noble gases were measured. These mass spectrometers were modified to be available for various extraterrestrial materials such as meteorites [1, 2, 3] and single micrometeorites [4].

Results and discussion

Prior to noble gas analysis, electron microprobe analysis revealed that marginal areas of the CAI were partly enriched in chlorine.

Noble gas analysis was performed in about 70 points in the CAI and neighbouring matrix. The chlorine-rich areas of the CAI have significantly high concentrations of ¹²⁹Xe than the chlorine-poor areas. Excess of ⁸⁰Kr produced by neutron capture on ⁷⁹Br correlated with the ¹²⁹Xe distribution. Several ¹²⁹Xe-rich points had relatively low ³⁸Ar/³⁶Ar ratios, which would be caused by the difference in cross section of neutron capture between ³⁵Cl and ³⁷Cl. The results show that the halogen-rich area was formed in a period when ¹²⁹I was still alive. Although we cannot determine the absolute time scale of the event when the halogens were enriched in some parts of CAIs, it must have occurred in the early stage of solar system formation.

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The geochemical impact of MSWI bottom ash on the environment

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Introduction

In Switzerland domestic waste without thermal treatment is no longer allowed to be stored in land fills. Consequently, the production of MSWI bottom ash has reached 650'000 tons per year, which have to be stored in special landfills. The present study is the first nation wide investigation to chemically and mineralogically characterize the bottom ash of all 27 incinerators. Special attention was also directed to the possibilities to separate metal fraction of the bottom ash using mechanical separation techniques, to recover metal fractions, to reduce landfill volume, and to evaluate possible changes to legislation for disposal.

Results and Conclusions

Regarding major elements the chemical compositions of the of the 27 bottom ash do not show big differences and are comparable to mafic/ultramafic rocks. Indicator for the different observed melting conditions can however be found using the Ca/Si ratio forming melilites and/or anorthite. Relatively small variation is observed for conservative behaving trace elements such as e.g. Zr which is rarely used in consumer products. Volatile elements such as Pb, Hg, and Cd are found as good indicators for thermal conditions of the incineration process, and C_{org} content for reaction time and temperature. Today's legislation prescribes bulk chemical analyses and leaching tests for the classification of e.g. "inert material" (TVA, 1990). In respect to inert material thresholds, some bulk metal concentrations are significantly elevated: Pb, Zn and Cu (3'000-40'000ppm). In contrast, leaching behaviour of the bottom ash in respect to TVA tests are mostly below legislation thresholds. To obtain better information about possible long-term behaviour of the residue in the hydrosphere, also alternative leaching tests have been adopted considering buffering capacity and leachability of trace metals under defined pH conditions.

Today still large amount of metals in waste enter incinerator plants, and most of them remain unaltered in the bottom ash. Using special mechanical treatment of the bottom ash, large amounts of ferrous metals, Cu, and Al could be separated in the fraction >2mm.

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Laser ablation-ICP-MS compositional profiling of chamber walls in planktonic Foraminifera; implications for Mg/Ca thermometry

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We have profiled compositional variation through the chamber walls of individual Foraminifera using a new, high resolution, laser ablation ICPMS technique. Mg/Ca ratios are able to be measured accurately and precisely in specific shell parts (wall layers and chambers) along with simultaneous analysis of other trace elements (e.g. Mn, Zn, Sr, Ba, Cd, U) and their isotopes with detection limits to low ng/g levels in <60 seconds. The mass of material consumed by each analysis is ~20-30ng (cf. typical test mass of ~10-30µg) and replicate analyses can be made on individual chambers. The technique readily distinguishes outer crust and inner primary wall layer compositions, as well as the presence of an outermost zone characterised by Mg, Mn, Ba and Zn concentrations increasing strongly towards the surface. Exploratory studies on planktonic Foraminifera (*Globigerina* and *Neoglobobulimina* sp.) define the capabilities of our technique, highlight the inherent limitations of conventional bulk analysis methods, and provide new insights into fundamental biomineralisation processes. Mg/Ca ratios can be reproducibly measured within particular chamber wall layers to ±2-5% and more uniformly distributed Sr/Ca ratios to ±1%. Inner primary wall layers of different chambers in the same test are commonly found to have distinct Mg/Ca compositions, whereas the inner portions of the outer crust on all chambers have similar and lower Mg/Ca. The strong enrichment in Mg, Mn, Ba, and Zn toward the outermost crust surface in both modern and fossil shells, suggests a significant vital effect change during the biomineralisation process. The ability to measure Mg/Ca in shell parts grown under specific seawater conditions, rather than bulk compositions integrated over the life-cycles of entire shells, may enable calibration of more accurate and precise Mg/Ca thermometers than is currently possible. The tiny amount of sample consumed also allows for subsequent δ¹⁸O microanalysis of the same shell material, and the simultaneous acquisition of other trace elements presents an opportunity to further develop their potential as proxies for seawater temperature, composition, and nutrient levels.

The structure of hematite (0001) surfaces in water: STM and resonant tunneling calculations of coexisting O and Fe terminations

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The structure of hematite (0001) surfaces is not fully understood; questions remain about the existence of Fe- and O- terminations of (0001) terraces. The presence or lack of Fe atoms at the (0001) surface that can be partially coordinated by adsorbed molecules is important for understanding a wide range of adsorption phenomena. We have imaged hematite (0001) surfaces in air and aqueous solution using STM and electrochemical STM (EC-STM), and interpreted images with the aid of a resonant tunneling model (RTM) parameterized using ab-initio calculations.

Our STM and RTM results are consistent with mixed O- and Fe-terminated (0001) surfaces (Figure 1). For surfaces that had been acid etched and extensively annealed, a periodic (period = 2.2 ± 0.2 nm) arrangement of O- and Fe-terminated domains was observed. Two different borders between domains should occur, one in which the Fe-termination is high relative to the O-termination and vice versa. These borders have significantly different heights, allowing us to conclude that the Fe-termination is topographically high on most terraces. Surface domains appear to be quite stable, with little evidence for dissolution at pH 1.

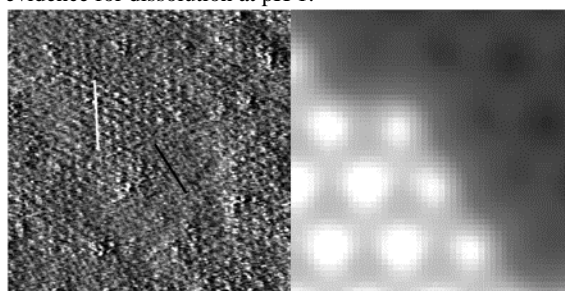


Figure 1: Two different domains in a 20x20 nm STM image of hematite (0001) (+500 mV; left) compared to an RTM calculation (2x2 nm) for +500 mV, Fe termination high.

Consistently, nonperiodic material is imaged at higher negative sample biases, and the characteristics of this material are consistent with resonant tunneling through "adsorbed" Fe atoms at the surface.

Apatite (U-Th)/He Signals of Transient Topography

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The influence of evolving topography on the exhumation history of mountain ranges has long been supposed but there have been few attempts to quantify the magnitudes of such interactions. We use a coupled atmospheric and surface process numerical model to quantify how the evolution of mountainous topography influences the cooling history of exhumed apatite (U-Th)/He thermochronometer samples.

Methods

The atmospheric model predicts orographic precipitation as a function of atmospheric moisture content, prevailing wind strength, temperature, and topographic slope (Roe et al., 2002). The coupled atmospheric and surface-process model predicts plan-form topographic evolution as a function of tectonic uplift, and processes of hill slope and fluvial erosional (Braun and Sambridge, 1997). Exhumed (U-Th)/He sample ages are calculated using multi-dimensional thermal models and a cooling-rate dependent model of helium diffusion in apatite.

Results

Model results indicate that orography is a first-order control on the topographic and exhumation history of mountain ranges. The model predicts that for a uniformly uplifting crustal block an orographically produced pulse of high erosion rates will propagate across the range in the wind direction and cause the drainage divide to migrate over time. This process of divide migration results in a trend of high to low rock exhumation rates across range in the wind direction. During the period of divide migration exhumed apatite (U-Th)/He sample ages are predicted to be youngest on the windward side of the range and increase towards the drainage divide. The topography eventually reaches steady state when erosion rates equal the exhumation rates across the orogen. Once the topography is in steady state the difference in exhumed apatite (U-Th)/He sample ages on the windward and leeward sides of the range decreases and spatial variations in ages occur only between valleys and ridges where exhumed sample cooling histories differ due to topography.

Conclusions

The coupled atmospheric and surface process model provides a climatic, geomorphic, and structural context for interpreting (U-Th)/He cooling, and cosmogenic exposure ages in areas with evolving topography. This study demonstrates that spatial variations in cooling ages can result solely from geomorphic processes and does not necessitate structurally controlled variable uplift rates.

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Complex organics and prebiotic molecules in space

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The connection between interstellar and solar system material is discussed from the perspective of recent laboratory studies testing the spectroscopic properties and photostability of large polycyclic aromatic hydrocarbons and prebiotic molecules. We discuss the life cycle of these molecules in extragalactic environments, the galactic interstellar medium, comets and meteorites.

U and Pb isotope ratios in manganese nodules by MC-ICP-MS

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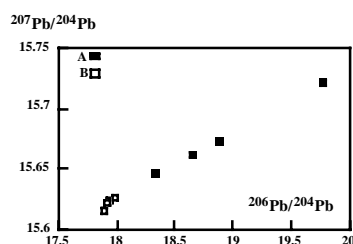
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Isotope ratios of U and Pb were measured in two groups of manganese nodules from the Cambrian Timna Formation, Israel. The division into two groups was based on petrographical, major and trace element geochemistry (Bar-Matthews, 1987). The first group (A) of nodules is composed mainly of pyrolusite and hollandite, with Mn, Ba, Pb and U concentrations of 45-50%, 1-2.5%, 0.1-0.8% and 500-3500 ppm respectively. The second group (B) was formed by alteration of the former, and contains mainly coronadaite, with Mn, Ba, Pb, and U concentrations of 9-30%, 0.2-5%, 1-2.5% and 60-150 ppm respectively.

Samples were dissolved in $\text{HNO}_3 + \text{H}_2\text{O}_2$ and measurements were obtained on the acid soluble fraction using the "Nu Instrument" MC-ICP-MS. Two sets of analyses were performed, with and without matrix separation. For Pb analyses, measurements were carried out with Meinhard nebulizer, and thallium ($^{205}\text{Tl}/^{203}\text{Tl}=2.3875$) was added to enable correction for mass discrimination. U was measured using an Aridus system with microconcentric nebulizer (MCN). Mass discrimination was corrected using U internal standard $^{238}\text{U}/^{235}\text{U}=137.88$.

The results obtained from the matrix-separated and unseparated samples were identical, with a slightly better (2σ) precision for the separated sample of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ 60-80ppm; $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ~30ppm and $^{234}\text{U}/^{238}\text{U}$ 0.2-0.4%.

The isotopic results support the distinction between the two groups. On a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot the nodules from group A have higher and variable ratios compared with the nodules of group B. Both groups fall probably on a mixing line (Fig. 1). $^{234}\text{U}/^{238}\text{U}$ in group A nodules fall close to the equilibrium values of 54.887 (Cheng et al., 2000), whereas in group B nodules the values fall usually below this value.



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Use of surface analysis, solid-state spectroscopy, and geochemical modelling to characterize phosphate-stabilized wastes

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Chemical stabilization of inorganic wastes can reduce leachability of heavy metals through formation of geochemically stable and insoluble precipitates. Understanding the immobilization reaction, the reaction products, and the leaching behaviour of the treated material is crucial for a mechanistic understanding of the process.

Our group has focused on phosphate stabilization of various MSW ashes, electric arc furnace dusts, smelter dusts, mine tailings, and metal-contaminated sediments. The approach typically characterizes both the untreated and the treated wastes before and after aggressive leaching with the Dutch NEN 7341 Availability Leach Test. A variety of bulk spectroscopic techniques (petrography, SEM-WDS, SEM-EDAX, XRD, STEM-XRM, MAS-NMR and EXAFS) are used to characterize untreated residues and metal phosphate reaction products. XPS is particularly useful in identifying surface species where leaching first occurs. SIMS can identify reaction mechanisms (sorption, surface precipitation to pre-existing phases, discrete phase precipitation) via depth profiling of discrete reactant particle agglomerates. pH-static leaching coupled with the geochemical thermodynamic equilibrium modelling with MINTQA2 can confirm chemical stabilization and solid phase control of leaching. MINTQA2 databases have been extensively modified to include many metal phosphate solids and ideal solid solutions for better applicability.

Immobilization mechanisms almost always involve precipitation of discrete metal phosphate crystalline solids or solid solutions. Apatite family (e.g., $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) minerals for Cd and Pb and tertiary metal phosphates (e.g. $\text{Zn}_3(\text{PO}_4)_2$) for Zn, Cu, and Cd are typical reaction products; these phases are very insoluble and are present after the treated residues have been subjected to aggressive leaching. Work is ongoing on the application of apatite-based reactive barriers for waste containment and plume interception.

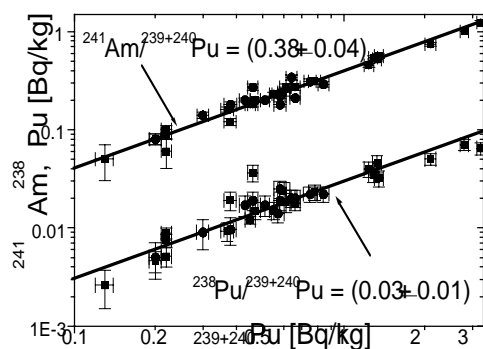
Actinide isotope analysis for determining different nuclear fallout components in soils

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The Swiss immission surveillance program around nuclear installation includes analyses of soil samples for various cosmic, terrestrial and particularly anthropogenic radioisotopes such as ⁷Be, ¹⁴C, ⁴⁰K, ⁸⁹Sr, ⁹⁰Sr, ¹³⁴Cs, ¹³⁷Cs, U- and Th-series decay products as well as the actinides ²³⁸Pu, ²³⁹⁺²⁴⁰Pu, ²⁴¹Pu, ²⁴¹Am, ²⁴⁴Cm. The isotopes of Pu and Am can be used to determine the fraction of hot particle fallout from different nuclear accidents, e.g. derived from surface atomic bomb tests in the 60ies or the Chernobyl accident, that occurred 16 years ago. Figure 1 shows that there is a strong correlation between ²³⁸Pu, ²⁴¹Am and ²³⁹⁺²⁴⁰Pu. The ²³⁸Pu/²³⁹⁺²⁴⁰Pu ratio of 0.03 ± 0.01 calculated via regression analysis agrees well with literature values obtained from various other sites in the northern hemisphere. For the ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratio a value of 0.38 ± 0.04 was obtained. This result is within uncertainty identical to the present day ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratio of 0.36 calculated via ²⁴¹Pu/²⁴¹Am progenitor/progeny relationship and additionally considering that the initial ²⁴¹Pu/²³⁹⁺²⁴⁰Pu ratio resulting from nuclear weapon testing in the 60ies was about 13. This result shows clearly that ²⁴¹Am measured in the samples analysed here can be well explained via support from decaying ²⁴¹Pu initially released during the surface A-bomb testing period meaning that contribution of heavy particles from the Chernobyl accident are not significant in Central Europe.

Figure 1: Correlation diagram with ²³⁸Pu vs. ²³⁹⁺²⁴⁰Pu and ²⁴¹Am vs. ²³⁹⁺²⁴⁰Pu obtained on Swiss soil samples from various locations.



Hydrogen-isotope geochemistry of the CM chondrites

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Hydration of initially anhydrous silicates and oxides is a common and significant early solar system processes recorded by the carbonaceous chondrites. We present new data constraining the hydrogen isotope geochemistry of the CM chondrites, which are characterised by a wide range in degree of hydration. Our study makes use of a recently developed method for analysis of D/H ratios of 10^{-9} mol quantities of water released by heating small (10's of microgram) solid samples.

Data for four CM chondrites (Murchison, Mighei, Murray, Cold Bokkeveld) document a trend of monotonically decreasing matrix D/H with increasing $[\delta^{18}\text{O}_{\text{matrix}} - \delta^{18}\text{O}_{\text{whole-rock}}]$ —a measure of the extent of aqueous alteration. The upper and lower limits in matrix D/H are 0.000148 (Murchison) and 0.000125 (Cold Bokkeveld). Mighei and Murray yielded intermediate D/H ratios of 0.000143 and 0.000137, respectively. A nearly anhydrous CM chondrite (L85311) was also analysed but was not sufficiently well resolved from background to yield a reliable D/H ratio. The D/H ratios of individual altered chondrules from both Cold Bokkeveld (highly hydrated) and Murchison (modestly hydrated) are equal to one another and to that for Cold Bokkeveld matrix; i.e., altered chondrules from both H-rich and H-poor samples have D/H ratios equal to that of the most extensively hydrated matrix. Replicate analyses suggest matrix is isotopically homogeneous within any one sample.

These data are not easily reconciled with either simple (0-dimensional) or chromatographic (1-dimensional) models of reaction between water and initially H-poor rock, in part because such models generally predict hyperbolic relationships between H-isotope composition and extent of aqueous alteration rather than the linear relationship we observe. Our results could be explained if the matrices of CM chondrites contained substantial amounts of hydrogen *before* they underwent the episode of aqueous alteration responsible for their first-order geochemical and mineralogical variations, or if they are mechanical mixtures of two components that did not share the same history of hydration and/or dehydration. Finally, our data suggest the D/H ratio of water that infiltrated the CM chondrites was ca. 0.000132. This value is interpretable as a constraint on the temperature at which infiltrating water last equilibrated with the dominant H reservoir of nebular H_2 ; this temperature was 282 ± 50 K if the D content of water was influenced only by $\text{H}_2\text{O}(v) - \text{H}_2(v)$ equilibrium and 390^{+110}_{-90} K if water was isotopically fractionated by formation of ice at a 'nebular snow line' before incorporation into the CM parent body. The principle source of uncertainty in these estimates is the protosolar D/H ratio (ca. 0.000034 ± 10).

Concentration and carbon stable isotope patterns of methane and DIC in deep peatlands – Implications for the microbial methanogenic pathways and gas transport

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Abstract

This study reports the results of a field study from October 1999 to August 2001 at the Etang de la Gruère (EGr) Bog in the Swiss Jura Mountains. Pore water samples were obtained in situ using diffusion chambers ("peepers") down to a depth of almost 6 m. Methane concentration of up to ca. 0.5 mM in the upper catotelm are comparable to those reported from shallow peat at other locations. Values continue to increase to almost 2.4 mM in the deep layers. The DIC concentration also generally increases with depth from ca. 1 mM in 0.5 m depth to up to 12 mM in 5 m depth. While DIC became less depleted in ¹³C with depth (ca. -22 ‰ vs. VPDB in the upper to ca. +9 ‰ in the lower catotelm), $\delta^{13}\text{C}$ values for pore water methane at EGr showed no straight trend with depth. Methane was isotopically light with $\delta^{13}\text{C}\text{-CH}_4$ values ranging from ca. -69 to -58 ‰ vs. the VPDB standard. The results indicate that CO₂-reduction represents a "background" microbial process, while the intensity of acetate splitting is much more variable depending mainly on temperature and the availability of acetate as metabolic substrate.

Significant seasonal variations can be inferred from concentration and isotope data for pore water methane in particular. These variations can be explained by the seasonal and depth-related change of the methane producing pathways: CO₂ reduction (lowest $\delta^{13}\text{C}\text{-CH}_4$ and high fractionation between CH₄ and CO₂) versus acetate splitting (higher $\delta^{13}\text{C}\text{-CH}_4$ and moderate CH₄-CO₂ fractionation). Transport processes such as pore water advection, molecular diffusion, and ebullition have a major impact on the concentration of the chemical species in depth/time space.

A numerical model adapted to the observations made at EGr indicates that gas transport by bubble formation is by far (maybe over 70 times) more efficient than diffusive transport. The discrepancies between model and field results underline the importance of the seasonality of labile organic precursor availability and over-saturation effects.

Kinetic Effects on Calcium Isotope ($\delta^{44}\text{Ca}$) Fractionation in Calcium carbonate

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The calcium isotope ratios ($\delta^{44}\text{Ca}$) of *Orbulina universa* and of inorganically precipitated aragonite are positively correlated to temperature. The slopes of 0.019 and 0.015 ‰ °C⁻¹ are a factor of 13 and 16 times smaller than the previously determined temperature dependence of 0.24 ‰ °C⁻¹ measured on *Globigerinoides sacculifer* (Näglér et al., 2000). The observed $\delta^{44}\text{Ca}$ fractionation is positively correlated to temperature. This fractionation is opposite to the oxygen isotopic fractionation ($\delta^{18}\text{O}$) which is inversely correlated to temperature in calcium carbonate (CaCO₃). This difference in sign is explained by a model that takes into account that Ca²⁺ ions, forming ionic bonds, are affected by kinetic fractionation only whereas covalently bound atoms like oxygen are also affected by equilibrium fractionation. From thermodynamic considerations it can be shown that the slope of the enrichment factor $\alpha(T)$ is mass dependent. However, the calculated mass for *O. universa* and the inorganic precipitates is about 640 amu (atomic mass units) which is not compatible with the expected ion mass for ⁴⁰Ca and ⁴⁴Ca. To reconcile this discrepancy we propose that Ca diffusion and Ca isotope fractionation at liquid/solid transitions involves the transport of Ca²⁺-aquocomplexes (Ca[(H₂O)₆]_n²⁺) rather than pure Ca²⁺ ion diffusion. From our measurements we calculate that such a Ca²⁺-aquocomplex correlates to a hydration number of up to 33 water molecules (Ca[(H₂O)₆]_{4.6}²⁺) although alternative complexation with other anions cannot be ruled out. The strong temperature dependence of $\delta^{44}\text{Ca}$ in *G. sacculifer* but weak temperature dependence in *O. universa* suggests considerable differences in their calcification mechanisms.

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Organic Contaminants in Lakes: Atmospheric Exchange and Linkage to the Trophic Status of Lakes

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Air-water exchange fluxes of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) have been determined in small lakes (ELA, Canada), the Great Lakes (Green Bay; Lake Michigan; Lake Superior) and in the estuaries of the Mid-Atlantic States (NY-NJ Harbor Estuary; Chesapeake Bay). In systems previously contaminated by PCBs, volatilization fluxes are large and play a dominant role in aquatic losses and as sources to the regional atmosphere. Other aquatic systems near urban-industrial centers experience enhanced deposition (absorptive fluxes) resulting from elevated concentrations in urban plumes. The controls and importance of air-water exchange of PCBs and PAHs in system mass balances and inventories, and in direct contamination of aquatic food webs will be discussed with examples from these well-studied systems. Air-water exchange of organic contaminants is an important if not dominant contributor to contamination of phytoplankton, the base of the aquatic food web, and thus is closely linked to carbon cycling and trophic status. In addition, improved physical-chemical properties of organic compounds and modeling frameworks permit the re-evaluation of organic chemical fluxes first determined 5 to 15 years ago, and their relative importance to total loads.

Various graphite morphologies with a diversity of C- and N-isotopic signatures in the highly equilibrated Acapulco meteorite

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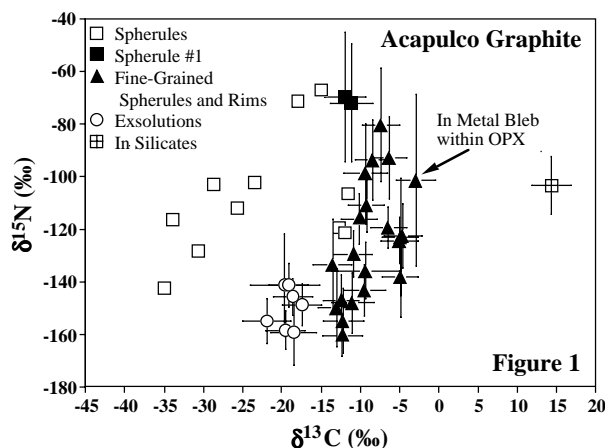
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Introduction

Acapulco is a highly equilibrated meteorite and a member of the acapulcoite-iodranite clan with strong chemical affinities to H-chondrites [1]. It has experienced partial melting and pervasive re-crystallization [1], a process expected to erase primordial N-isotopic signatures.

In a detailed petrographic-isotopic study of graphite in this meteorite we encountered eight different graphite morphologies, either in close vicinity or inter-grown with each other. These include spherulitic, feathery, fibrous bands, round fine-grained inclusions, exsolution veneers between kamacite and taenite, and single crystals in the silicate matrix. The C- and N-isotopic ratios ($\delta^{13}\text{C}$ versus $\delta^{15}\text{N}$) are plotted in Figure 1. Spherulitic graphite plots along a linear array with a slope of 3.25. Graphite exsolution veneers at the kamacite-taenite interface has the lightest C- and N-isotopic compositions ($\delta^{13}\text{C} = -23 \rightarrow -18 \text{‰}$, $\delta^{15}\text{N} = -159 \rightarrow -141 \text{‰}$). Fibrous graphite band around spherulitic graphite has much lighter N than the spherulitic core ($\delta^{15}\text{N} = -145 \text{‰}$ versus $\delta^{15}\text{N} = -71 \text{‰}$). A single crystal in the silicate matrix has an C-isotopic ratio completely different from all other graphite grains in Acapulco (Figure 1).



The results indicate that the individual graphite morphologies retained their pristine isotopic signatures, despite the pervasive equilibration and partial melting experienced at $T = 1200^\circ\text{C}$ by the Acapulco parent body [1].

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Geochemical response to arc-continent collision on Alor, Sunda-Banda arc, Indonesia

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The island of Alor lies in the extinct sector of the Sunda-Banda arc, where collision with the Australian continent halted subduction-related volcanism. It provides us with an end member scenario of arc magmatism, where the geochemistry is dominated by input from the subducting plate.

Older lava flows and intrusives (2.5 Ma) have rather homogeneous geochemical characteristics, with only moderately 'crustal' signatures ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7060\text{-}0.7066$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.51261\text{-}0.51252$, $^{206}\text{Pb}/^{204}\text{Pb} = 19.1\text{-}19.2$).

The youngest volcanic deposits (1.3 Ma) show extreme isotopic variability ($^{87}\text{Sr}/^{86}\text{Sr} = 0.706\text{-}0.711$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.5126\text{-}0.5122$) with Pb isotope ratios among the highest recorded for an island arc ($^{206}\text{Pb}/^{204}\text{Pb} = 19.0\text{-}19.6$; $^{208}\text{Pb}/^{204}\text{Pb} = 39.3\text{-}40$). The highest Pb isotope ratios are only found on the north coast (distal from the trench), and the extreme $^{208}\text{Pb}/^{204}\text{Pb}$ ratios reflect subduction of upper crustal material of Australian origin. Some south coast samples combine higher Sr with lower Pb isotopic characteristics, indicating that the isotopic composition of the youngest deposits cannot be explained by two component mixing of mantle and subducted sediments. The lower-Pb isotopic component resembles cordierite-bearing samples of the neighbouring island Wetar, suggesting an origin in the lower (?) continental crust.

Trace elements ratios such as Pb/Ce indicate that any influence of a fluid component in the source of the youngest volcanics is masked by the large amount of subducted continental material. High Th/Nb ratios for the high $^{206}\text{Pb}/^{204}\text{Pb}$ samples indicate that the slab to wedge transfer medium was a partial melt, but this may not be the case for the samples with lower Pb isotopic signatures.

Conclusions

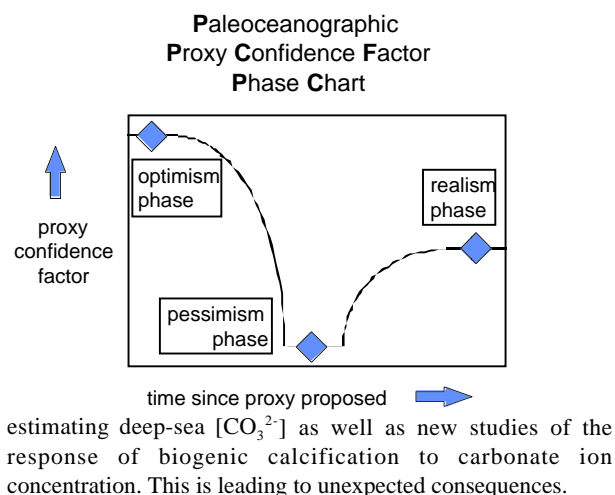
Our results show that arc-continent collision results in isotopic signatures becoming more heterogeneous, reflecting subduction of continental crust and, in the case of Alor, addition of two types of crustal material to the mantle wedge. This situation contrasts with the active part of the Sunda-Banda arc where only one type of crustal material is added to the mantle wedge, and where a fluid component plays an important role in frontal volcanoes.

Foraminiferal Mg/Ca paleothermometry: expected advances and unexpected consequences

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"The oxygen isotope method of determining paleotemperatures (Urey H., *J. Chem. Soc.*, 562, 1947) is widely regarded as a tool of unique potential in the investigation of past changes in the temperature of the earth's surface." (Shackleton N.J., *Colloq. Int. Cent. Natl.*, 219, 203, 1974). That potential was first realised by Epstein S., Bushsbaum R., Lowenstam H.A. and Urey H. (*Geol. Soc. Amer. Bull.*, 62, 417, 1951; *ibid* 64, 1315, 1953) and its subsequent development has played an invaluable role in paleoclimate research. Among the newer methods for estimating paleotemperature (including faunal analysis and alkenones), Mg/Ca thermometry has the added potential, not yet realised, of providing an estimate of seawater $\delta^{18}\text{O}$. Like all proxies, it is moving through the PPCFPC (see graph). This development has the added benefit that more is being learned about $\delta^{18}\text{O}$ systematics as well as the factors controlling trace element incorporation and retention in marine biogenic carbonates. Amongst these, the influence of dissolution on Mg/Ca is a matter of current importance and has interesting links with recent ideas for



Li isotope variations in the upper mantle

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A large proportion of the mantle is likely to have been re-enriched by recycled oceanic lithosphere, such as envisioned by the marble cake mantle. Yet definitive evidence for such recycled material, despite the host of distinctive geochemical signatures it is expected to impart, remains elusive. Partly as a consequence, alternative theories have become popular in which subducted slabs form a deep, hidden reservoir and are largely removed from our mantle sample.

A novel means to address this issue is the use Li isotopes. Alteration of the oceanic lithosphere both increases its Li concentration and ⁷Li/⁶Li. Mixing of this material back into the upper mantle should therefore elevate its ⁷Li/⁶Li and generate Li isotope heterogeneity on a small scale. New Plasma Induced Multi-collector Mass Spectrometers (PIMMS) dramatically improve the reproducibility of Li isotope measurements. Analyses with the Finnigan Neptune allow us to determine natural variations in ⁷Li/⁶Li of less than 0.5 per mil, using rapid sample-standard bracketing. Using this enhanced analytical capability, we have begun to investigate ⁷Li/⁶Li variations in well characterised basaltic glasses from the East Pacific Rise (10.5 and 11.5°N). Initial results show a significant spread in ⁷Li/⁶Li of ~1.5 per mil. The Li isotope variation correlates with ⁸⁷Sr/⁸⁶Sr and La/Sm, but not [Li] or MgO, suggesting it is a primary signature. It thus appears that a definitive signature of recycled material in the upper mantle has been gleaned.

Lipid biomarkers as a tool for the analysis of anaerobic methanotrophy in marine environments

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Downcore lipid analysis of gas hydrate-bearing sediments at Hydrate Ridge and methane-rich sediments from the Håkon Mosby Mud Volcano (HMMV) show elevated concentrations and high numbers of diverse membrane lipids (biomarkers) of archaeal and bacterial origin. Structural and carbon isotopic analyses demonstrate the presence of a consortium of archaea and sulfate-reducing bacteria oxidizing methane under anoxic conditions. Concentrations of relevant biomarkers are clearly enriched at locations with elevated methane seepage and decreased at locations with lower methane outflow. The enrichment of consortium-specific biomarkers is directly translated into their isotopically light carbon isotopic signature. Concentrations and carbon isotopes are in good agreement with rate measurements and rRNA analyses and thus help identifying the methane oxidation zones *in situ*. Whereas high methane oxidation rates at Hydrate Ridge can be found throughout the core, methane oxidation at HMMV takes place only in a restricted zone right below the sediment surface. Small increments may, however, indicate a second *hot spot* of anaerobic methanotrophy or, on the other hand, active methanogenesis in deeper layers. Among the specific biomarkers, isoprenoids (crocetane, pentamethylcosenes) and glycerolethers (archaeol, hydroxyarchaeol) are identifiable as markers of the archaeal partner belonging to the *Methanosarcinales* group. The most dominant biomarkers of bacterial origin are monoalkylglycerolethers containing hexadecyl carbon chains and the fatty acids cis11-C_{16:1} and ΔC_{17:0}. These biomarkers can be attributed to the syntrophic bacterial partner closely related to the *Desulfosarcina-Desulfococcus* group.

Hypotheses and facts on the when, why and how of sapropel formation in the Mediterranean Sea

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Sapropels in the Mediterranean Sea are sediment layers that were deposited during periods when the deep waters of the eastern Mediterranean Sea were anoxic for several thousands of years. Anoxia was caused by enhanced water column stratification. I review the state of knowledge on three aspects of sapropel formation: the timing of sapropels and implications for the underlying climatic mechanism, the causes for stratification and geographical patterns of run-off, and the coupled chemical and biological consequences that led to enhanced organic carbon accumulation.

Differing from previous hypotheses, recent investigations on speleothems suggest that enhanced rainfall and onset of anoxic conditions were synchronous with insolation maxima. Large negative excursions in $\delta^{18}\text{O}$ in sapropels are largely accounted for by increasing SST and pooling of isotopically depleted water in the surface layer. Spatial patterns in coeval sapropels are consistent with climate processes in the low latitude catchment and of regional surface water warming associated with insolation cycles. However, much of the excess moisture apparently originated from evaporation in the Mediterranean Sea.

Regional and global temperature evolution modulated the basic sapropel rhythm and raised the threshold for full stagnation of deep water during glacials, but each insolation-related swing from cold to warm and from dry to wet conditions is expressed as a "failed sapropel" in the isotopic, chemical, and faunal records.

Increased accumulation of organic matter was a consequence both of higher productivity and enhanced preservation of organic matter. Both were caused by anoxic conditions at the sea floor. Very low (-1 to 1‰) $\delta^{15}\text{N}$ ratios in sapropels require a very light source of nutrient-N assimilated at a minimum of ten times the modern export flux. Because isochronous records show no spatial gradient in the $\delta^{15}\text{N}$, we may exclude both Ekman-type upwelling and direct riverine discharge as likely sources of nutrients. Instead it appears that phosphorus release from sediments and denitrification at a relatively shallow redox boundary resulted in an imbalanced supply of nutrients (N:P < 16:1) to the photic zone. The result was a slow assimilation of carbon during summer stratification and extensive N_2 -fixation providing the majority of the export flux from a N-limited system.

Sapropels thus result from a basic mechanism operating in all silled basins of the temperate climate zone at transitions from cool to warm climate. The robust relationship between climate, surface water properties and biological consequences seen in the Mediterranean Sea is an analog for many black shale events of the geological record.

Element contents in the ash of dropwort roots and in the soil around the roots

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Biogeochemical mapping for characterising the pollution of the environment with heavy metals and other hazardous elements has been carried out in Estonia using dropwort (*Filipendula Ulmaria*) roots as indicators. Dropwort was chosen out, because this plant met the requirements established for indicator plants. Compared with geochemical mapping of soil, biogeochemical investigations give an overview of elements which are collected from the soil that surrounds the growing plants.

The aim of this investigation was both identifying the possible pollution of soil with a biogeochemical method, and analysing soil from the same sampling points where dropwort roots were collected.

50 sample pairs collected from the same sampling points have been compared. Root samples were washed, dried and ashed at 450°C. Analysed were Cd, Cu, Fe, Mg, Mn, Pb and Zn by AAS, P by colorimetric and Nb, Rb, Sr and U by XRF method. In soil samples the same elements were analysed with the same methods.

Results will show that the elements Cd, Cu, Mg, Mn, Nb, P, Rb, Sr, Zn and U concentrate better in dropwort roots than in soil. These results show how intensively plants collect nutrient elements from the soil. It became evident that the anomalies in the analysed results can be caused by pollution in the surrounding soil, higher concentrations in bedrock but also by anthropogenic pollution.

Plants are more sensitive for identifying pollution. Plants show pollution from a whole catchment area, but soil only pollution in a certain sampling point. The heterogeneity of the soil in both vertical and horizontal layers interferes with a good comparison of the results; in this case plants are better indicators for the environment.

Biom mineralization mechanisms in foraminifera and corals and their paleoceanographic implications

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Foraminifera and corals CaCO₃ shells are highly valuable for paleoceanographic reconstructions. However, their complex biomineralization process, often cause significant deviations from expected chemical and isotopic equilibrium. Our new observations on the calcification mechanisms in foraminifera and corals are based on various microscopic techniques including light, fluorescent, spectral, confocal and electron microscopy. They show several basic features that are common for both groups: Crystal nucleation and growth are mediated by an organic matrix. The shells consist of two types of crystals, primary and secondary, which have different chemical compositions (usually more enriched in trace elements). The solution from which calcification proceed is seawater, which may be slightly modified in its ionic composition. This seawater calcification reservoir is maintained at high pH. The calcification reservoir is behaving as a semi-closed system with respect to trace elements distribution coefficients. Seawater in the calcification reservoir is replaced by intensive vacuolization in foraminifera and by tissue pumping in corals. The implications of these observations for paleoceanography are far reaching. The "good news" is that for their secondary calcification (responsible for more than 90% of the CaCO₃ in their shell), foraminifera and corals start with ambient seawater as their initial ingredient. Apparent distribution coefficients arising from this semi-closed reservoir can be modelled. Primary calcification in both groups is strongly controlled by the organism in close association with the organic matrix. The primary crystals may significantly deviate from equilibrium (especially with respect to trace elements and stable isotopes in foraminifera). The proportions between these two components and their apparent different solubility may determine the overall chemical and isotopic composition of the shell.

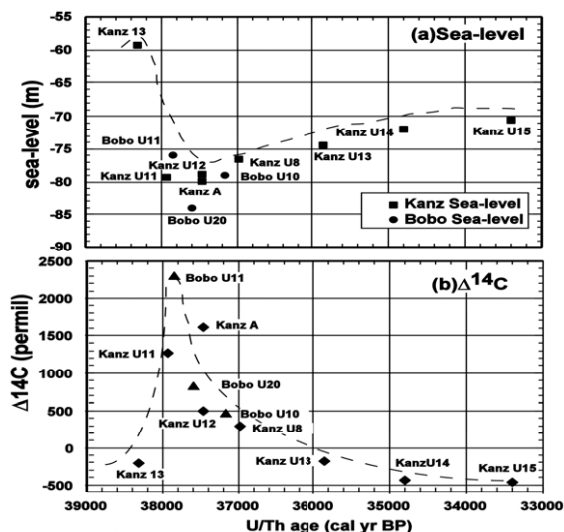
Rapid sea-level, ice-volume and radiocarbon excursions during a Heinrich event at Huon Peninsula

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We have previously demonstrated a connection between the ages of OIS-3 coral terraces at Huon Peninsula and the timing of North and South Atlantic ice-rafted debris layers and hence Heinrich events. In addition, coral radiocarbon analyses revealed large radiocarbon peaks at the same time periods which can best be explained by the stop-start behaviour of the thermohaline circulation. One of the better documented ¹⁴C peaks occurs at ≈38 ka and was derived from corals of terrace IIa, a prominent reef both at Bobongara and Kanzarua. In the figure, we have plotted the sea-level curve and excess ¹⁴C on the same time scale. The phase relationship between the various events is as follows: Just before 38.3 ka and sea-level



is at its peak. Terrace IIa crest is in place. Over the next 1000 years the sea level drops by over 20 m. The radiocarbon levels rise rapidly and reach their peak within 500 years at 37.8 ka. Presumably, the Gulf-stream slowdown occurs before 38.3 ka and by 37.8 ka the circulation is again active. The radiocarbon levels drop to previous values within about 2000 years and decline further over the next 3000 years, possibly indicating a vigorous re-start to the circulation. The data demonstrate the rapidity of the sea-level changes and by implication the rapidity with which ice-sheets can partially disintegrate and recover. Equally sharp is the 230% excess atmospheric radiocarbon pulse.

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Organic chemistry and the riddle of the pre-RNA world(s)

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The lecture will survey experimental contributions to the pre-RNA-world problem from past and current organic chemistry and will focus on recent results obtained in the author's laboratory.

Os, Sr, Nd, Pb isotopic systematics in basalts and carbonatites from Fogo Island, Cape Verde

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Previous trace element and isotope data of basalts from Cape Verde archipelago have shown a difference between the northern and southern islands.

Here we focus on Fogo island (southern group) and report Os-Sr-Nd-Pb systematics on 17 basalts and 2 carbonatites. Except one sample, basalts present ¹⁸⁷Os/¹⁸⁸Os ranging from 0.13197 to 0.13694 and concentrations from 4.8 ppt to 28.6 ppt. Sr-Nd-Pb isotopic compositions are in the southern island range [1,2,3]. Basalts define positive correlations in lead-lead diagrams and negative correlations in Pb-Sr and Sr-Nd diagrams, significantly steeper than the classical mantle array in the latter. These correlations are interpreted as a mixing between a moderate 'high μ ' end-member and an enriched end-member identified as Sub-continental lithospheric Mantle (SCLM). Os isotopic data coupled with other systems show unexpected negative Pb-Os and positive Sr-Os correlations that imply radiogenic ¹⁸⁷Os/¹⁸⁸Os for the EMI-like end-member.

Both carbonatites present similar isotopic composition with ¹⁸⁷Os/¹⁸⁸Os = 0.17; ⁸⁷Sr/⁸⁶Sr = 0.703158; ¹⁴³Nd/¹⁴⁴Nd = 0.512930; ²⁰⁶Pb/²⁰⁴Pb = 19.5; ²⁰⁷Pb/²⁰⁴Pb = 15.597; ²⁰⁸Pb/²⁰⁴Pb = 39.189. Such compositions do not plot on the basalt correlations, precluding carbonatite fluid as the moderate 'high μ ' end-member. We rather propose a mixing between a 1.6 Ga recycled oceanic crust and lower mantle material.

Comparisons with trace element and Sr-Nd-Pb isotope data of kimberlites and lamproites suggest that the SCLM involved in Cape Verde source has encountered enrichment in incompatible elements by melt percolation. Such feature and recent works [4,5] on Canary islands lead to propose a partial melting model of SCLM that can generate the whole isotopic composition required for the enriched end-member, especially ¹⁸⁷Os/¹⁸⁸Os up to 0.14, consistent with the unradiogenic Os isotopic ratios of peridotite xenoliths.

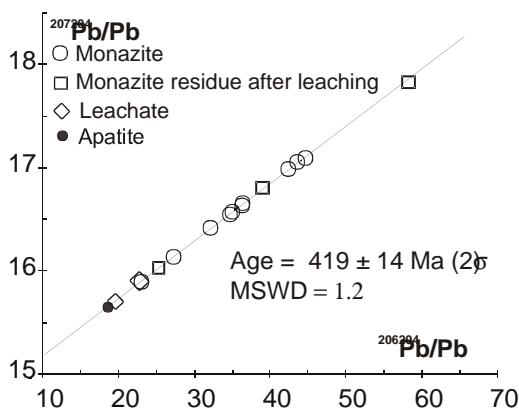
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Dating diagenetic monazite in mudrocks: constraining the oil window?

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Authigenic monazite nodules, increasingly recognised in Pre-Mesozoic mudrock successions, provide a means for dating diagenesis by exploiting trace uranium within the monazite structure. But, dating is difficult in practice because of zonation and abundant host rock inclusions. We report here a refined technique that has yielded a date of 419 ± 14 Ma 2σ MSWD = 1.2 for a 17-point Pb-Pb regression age from a Telychian (Silurian: late Llandovery c.430 Ma) mudrock from central Wales.



SHRIMP analyses of the same material are consistent with this, and additionally demonstrate concordance of the U-Pb and Th-Pb systems. These results open the door to providing robust dates for a phase of burial related diagenesis, which, in Wales, seems approximately coincident with hydrocarbon expulsion.

Determination of variations in isotope ratios of Hg

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The question of whether Hg isotopes are fractionated to a measurable degree in natural environments by chemical, physical and biological processes remains unanswered. If isotopic signatures of Hg from various anthropogenic sources or environmental compartments are different, it may be possible to fingerprint Hg, partitioning accumulated Hg according to source.

Recent development of multicollector-ICP-MS (MC-ICP-MS) instruments makes it possible to measure isotope ratios of Hg with high precision. MC-ICP-MS has been used primarily in geological applications, and only recently has its potential for environmental applications begun to be explored. Measurement of high precision isotope ratios in environmental matrices presents a different set of challenges. Given the low concentrations of Hg in environmental media and the very small differences between ratios that we expect to find, sample introduction without contamination is a major problem to be overcome.

Mercury can be introduced to the MC-ICP-MS as a liquid, or vapour via hydride generation or directly after trapping and thermal desorption on gold traps. Each of these techniques has limitations with respect to isotope ratio measurement. We will discuss some of these limitations. Our preferred approach is the gold trapping method. As will be demonstrated, this technique minimizes potential for sample contamination. The major drawback is the necessity to work with transient signals, usually considered detrimental to measurement of high precision isotope ratios. However, our work suggests that acceptable precision can be achieved using transient signals, while maintaining the veracity of the original isotopic signature.

Hg isotopic signatures vary by more than 1‰ per AMU across a range of sample types. However, the differences are very small, and external variation among replicate samples is high. In part, this variability is attributable to the transient signals. The potential for blurring of signatures from external contamination remains a serious issue. Further work will be required to develop simple, standardized methods for Hg isotope ratio determination.

Developments in Fluorite (U-Th)/He Thermochronology

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We report the results of (U-Th)/He dating trials on fluorite precipitated as a secondary hydrothermal mineral within Miocene tuff (12.8 Ma) at Yucca Mountain, Nevada.

Three varieties of fluorite crystals were separated from vein specimens containing 1–3 mm thick layers of fluorite. Early fluorite adjacent to the host tuff is translucent, changing gradually to colourless and finally purple transparent varieties. Several mg of 100–300 µm, inclusion-free crystals were analysed from the three varieties. The cloudy crystal layers adjacent to the tuff have (U-Th)/He ages of 9.8 ± 0.3 Ma. The clear fluorite is slightly older (11.9–15.6 Ma), whereas the purple grains consistently yield anomalously high He contents resulting in geologically unreasonable ages.

Fluorite	U (ppm)	Th (ppm)	Age (Ma)	$\pm 2\sigma$
purple	6.5	1.4	212, 41	1.1
clear	10.6	0.22	11.9, 13.8, 15.6	0.4
cloudy	12.1	0.64	9.7, 9.9	0.3

Alpha-emission correction after Farley et al., (1996). Mean U and Th concentrations given.

He diffusion experiments were carried out at Caltech on a handpicked sample of 200–350 µm colourless fluorite. The helium closure temperature for this fluorite is 60 ± 5 °C, assuming a 10 °C/Ma cooling rate. The (U-Th)/He age of 9.8 Ma for the cloudy variety of fluorite indicates that it was precipitated within 2 myr of tuff deposition. Subsequently, only meteoric fluids cooler than 35 °C entered the site (Wilson et al., submitted). We suggest that the purple variety was in contact with late-stage U-rich fluids that implanted He in the fluorite margins and caused discoloration of the crystals.

Material properties and microstructure from Crystallisation of (PGE)AsS from sulphide melt

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Amongst Platinum-Group Minerals (PGM) there are sulpharsenides of all Platinum-Group Elements (PGE) except Pd: platarsite, PtAsS; irarsite, IrAsS; hollingworthite, RhAsS; osarsite, OsAsS; ruarsite, RuAsS. The 'ideal' composition corresponds to the end members, 'PGE'AsS, but the real ones present the intermediate members of solids solutions regarding to PGE and As-S.

PGE sulpharsenides are found in basic/ultrabasic complexes with chromite or cooper-nickel sulphide mineralization, i.e. ophiolites, layered intrusions etc. Essentially all PGE sulpharsenides occur in metamorphosed rocks and ores. But the conditions of their formation remain unknown. The (PGE)AsS bearing associations could contain other PGM and basic sulphides. Very often people find the crystal of 'PGE'AsS in close association with Ni-rich sulphides, as millerite, and heazlewoodite. For example, Shetland ophiolites contain: 1) IrAsS + RuS₂+Os, 2) IrAsS + RuS₂, and 3) IrAsS + RuS₂ + Ru-bearing pentlandite (Ni>Fe). Noril'sk Cu-Ni sulphide ores present other associations: RhAsS + CuFeS₂ + (Fe,Ni)₆S₇ (+Ni₈S₈), or RhAsS + CuFeS₂ + NiS + (Ni,Fe)₉S₈. It seems to be interesting to check the possibility of 'PGE' sulpharsenide formation directly from the sulphide melt containing Cu, Fe, Ni, and PGE.

Based on the composition of natural associations the preliminary experimental study was carried out in evacuated quartz ampoules. 100 mG charges of elements corresponded to the mixtures: 1) 'PGE'AsS + Po_m+Pn_{Ni}+Cp, 2) 'PGE'AsS + Cp + Bor + Pn_{Ni} + Mil, and 3) 'PGE'AsS + Cp + Tr +Pn_{Fe}, in different proportions. Charges were preheated in the argon flow (400 °C), then gradually heated to 1080 °C, annealed at this temperature during 76 hours, and slow cooled with the furnace. Polished sections from samples synthesized were studied with optical microscope, microprobe, and electron microscope (SEM + energy disperse analysis).

In spite of the relatively low proportion of 'PGE'AsS in the charges (~10 mol.%) some 'PGE' sulpharsenides were crystallized, i.e. RhAsS in association with Cp and Pn_{Ni}, and with Cub and Po_m, and IrAsS with Cub. The most of other PGM are dispersed in basic sulphides, but the additional study is necessary to determine the form of their occurrence: isomorphous elements in sulphide structures or tiny inclusions in sulphide matrix.

Using the composition of associated sulphides the conditions of 'PGE'AsS formation (i.e.) are discussed relative to the stability of basic sulphides. For both, RhAsS and IrAsS, $I_{g,IS2}$ is less than 10 at $T < 600$ °C that is in agreement with experimental data of one of the author on the stability field of some other PGM.

Impact of the Nuclear Fuel Cycle on the Environment

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The nuclear fuel cycle impacts two types of geochemical cycles: **Carbon cycle**: reduced emissions of carbon to the atmosphere as nuclear power plants replace carbon-based sources of energy. **Radionuclide cycles**: increased production of technogenic radionuclides in spent nuclear fuel (SNF). Depending on national policy, the SNF is considered a waste product, or fissile nuclides, such as ²³⁵U and ²³⁹Pu, can be recycled for further energy production. However, most fission products and the “minor” actinides (Cm, Am, Np) are generally considered waste. Unlike other energy producing systems, the by-product, fissile nuclides, can be diverted for weapons production. This paper analyzes the global impact of increased utilization of the nuclear fuel cycle.

Carbon Cycle: In Kyoto, a Framework Convention on Climate Change proposed a reduction of greenhouse-gas emissions of industrialized countries by 5 percent below 1990 levels, over the next ten to fifteen years. However, energy demands world-wide are increasing and are expected to at least double over the next fifty years. The amount of energy supplied by carbon-free sources must grow by a factor of ten to twenty by 2050 (Fetter, 2000). At present, the use of nuclear power plants avoids carbon dioxide emissions of an estimated 600 million metric tons per year. However, in order to impact carbon emissions in a significant way by 2050, electrical power production by nuclear plants would have to reach 3,300 gigawatt-years (a single GW-year is the output of a large electric power plant) (Sailor et al., 2000). Even if the installed capacity of nuclear power plants only reaches 1,000 GW, there is the potential to avoid the emission of 6 billion metric tons of CO₂. Although this number is large, it has to be evaluated in the context of carbon exchange fluxes and sinks between the atmosphere, land and oceans.

Radionuclide Cycles: Although the use of nuclear power plants to produce electricity will reduce CO₂ emissions, there will also be a concomitant increase in the production of SNF and high-level nuclear waste. In 2002, approximately 150,000 metric tons of SNF have already accumulated. One of the principal concerns is the production of technogenic radionuclides, such as the transuranium elements, particularly Pu. There is presently a global inventory of over 1,400 metric tons of Pu. At present, the annual production of spent nuclear fuel is on the order of 10,000 metric tons (containing approximately 100 metric tons of fissile Pu). A ten-fold increase in nuclear power plants will yield substantial quantities of spent nuclear fuel, approximately 100,000 metric tons per year (for comparison, the legislated capacity for the proposed geologic repository at Yucca Mountain is 70,000 metric tons of SNF).

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