

P-T-t history of granulites from the Schirmacher Oasis, East Antarctica

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Granulite facies rocks in the Schirmacher Oasis, Central Dronning Maud Land, East Antarctica consist of metapelites (Qtz + NaKfs + Pl + Sil + Grt + Rt + Phl ± Zn Spl) intruded earlier by metanoritic dykes and metagabbro (Opx1 + Pl1 ± Cpx1 ± Grt1 ± Prg ± Ilm ± Qtz) and later by enderbitic gneiss and metamafic dykes (Opx ± Cpx1 + Pl + Ilm ± Qtz ± Kfs) – all multiply deformed and metamorphosed. Reaction textures (Ravikant and Kundu, 1998) and geothermobarometric studies on these rocks indicate two distinct stages in their P-T evolution – a prominent essentially isothermal decompression from 8±1 kbar, 800±50 °C to 5±1 kbar, 700±50 °C and near isobaric cooling evident from growth of coronal garnets in many of the rocks.

Sm-Nd isochrons based on whole rocks and minerals (mainly coronal garnet) of the enderbitic gneiss give indistinguishable ages (616±52 and 632±8 Ma, 2σ errors) and initial Nd isotopic ratios ($\epsilon_{Nd} = 0 \pm 0.04$ and 0.25 ± 0.28), respectively. While the similarity in the wholerock and mineral ages indicates that the above two stages occurred sequentially within a short interval at about 630 Ma, the near chondritic initial Nd isotopic ratios suggest derivation of dioritic magma from a crustal mafic source formed much earlier, probably ~ 1.2 – 1.0 Ga (Jacobs et al., 1998; Moeller et al., 1998).

The remarkable similarity in the timing (~ 630 Ma) of high-grade metamorphic events both in the Lurio Belt, Africa (Kroner et al., 1997) and the Schirmacher Oasis, Antarctica supports their spatial continuity before breakup of the Gondwanaland as proposed by Shackleton et al., (1997).

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Geochemistry and pollution of groundwaters from the north-western side of Campi Flegrei caldera (Naples, Italy)

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Introduction

The concentrations of major and minor ionic species have been detected in groundwater from the north-western side of Campi Flegrei caldera (Naples, Italy). In attempting to define the role of agricultural pollutants as groundwater contaminants we focused particular attention on the distribution and speciation of nitrogen in sampled waters.

The circulation of shallow water occurs through volcanic pyroclastic levels. Because of the vertical and lateral variations in granulometry, constipation and lithification of the volcanites, the shallow aquifer result to be subdivided in superimposed strata, which result to be separated by relatively impermeable volcanic levels.

Water geochemistry and pollution

On the base of geochemical data three zones can be individualized south of Patria lake: I-zone around the lake: Ca-bicarbonate waters circulating in a very shallow stratum, II-zone moving to the south: alkali-bicarbonate waters coming from a deeper aquifer fed by meteoric supply, III-zone, in the south-eastern part of the studied area: alkali-sulphate chloride waters which composition indicate a different source (probably the presence of a volcanic-magmatic component) and a different pathway of waters into the aquifer. Among the three zones some differences have been found: I-zone: nitrates are under the EC limits for drinking waters (50mg/l), no ammonia or nitrites have been detected; II-zone: nitrates are generally under the E.C. limits and little levels of ammonia and nitrites have been found, only in some samples nitrates exceed fixed limits; III-zone: nitrates are under the E.C. limits for all but one sample showing very high nitrate contents (112.56 mg/l).

Tab. 1: mean pH and temperature values and concentration ranges (mg/l) of ionic species by waters type.

Water type	No. of samples	pH	T°C	NO2	NO3	NH4	F
1	4	7.21	19.5	ab.*1	9.11	tr.*2	1.46
2	23	7.03	18.3	0.20	30.3	0.12	2.59
3	5	7.67	19.3	ab.*1	30.1	ab.*1	8.94

1: Ca-bicarbonate waters; 2: alkali-bicarbonate waters; 3: alkali-sulphate chloride waters. *1ab.=absent; *2 tr. =trace

Data show that generally the aquifers result to be isolated with respect to the superficial agricultural pollution. In some cases abnormally high nitrates contents indicate the presence of wells in which filtrate contaminated waters from the surface.

Zircon Evidence of the Earliest Archean Crust: 4.0–4.4 Ga

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Detrital and xenocrystic zircons from 4 locations in the Yilgarn craton (W.A.) have U-Pb ages older than 4 Ga, the oldest is 4.404 Ga. These crystals are older than any dated terrestrial rock and provide our only solid evidence of the earliest Archean. The search for parent rocks is on-going (see Cavosie et al., this volume). Single crystals in one suite of detrital zircons from the Jack Hills metaconglomerate, including the oldest zircon, have been analyzed for age, (18O, and REEs by ion probe. Zircons are HREE enriched to 10,000x chondrite with positive Ce and negative Eu anomalies. Calculated magmas are LREE-enriched. CL imaging shows concentric growth zoning. Some zircons have correlated REE and (18O variation. The 4.4 Ga zircon measures $\approx 100 \times 220$ (m and contains 1-20 (m inclusions of quartz and 0.4 – 1.0 (m inclusions that may be K-feldspar \pm qtz, albite, magnetite, and pyrite. Thus the parent magma was differentiated, quartz saturated and probably granitic (or rhyolitic), consistent with continental crust. Values of $\delta^{18}\text{O}$ range from 5.0 to 7.4‰ VSMOW. This range in $\delta^{18}\text{O}$ is the same as for younger zircons throughout the Archean, consistent with a similar genesis. Four crystals have $\delta^{18}\text{O}$ higher than in mantle melts, suggesting crystallization in a magma formed by burial and melting of protoliths elevated in $\delta^{18}\text{O}$ by interaction with low temperature fluids near the surface of the Earth (i.e., hydrothermal alteration, diagenesis, or weathering). While considerable uncertainty exists for many aspects of the early Archean, the best interpretation of these results is that liquid water existed on the surface of the Earth at least intermittently from 4.0-4.4 Ga. If the hydrosphere was similar to today, temperatures are indicated below 200°C (to elevate $\delta^{18}\text{O}$ in protolith) with buffered atmospheric P(H₂O). Taken together, these results suggest rapid cooling of the Earth following accretion, and formation of the Moon and core. The flux of meteorite bombardment may have decreased more rapidly than previously thought permitting a “cool early Earth” from ca. 4.0 to 4.4 Ga. We are not aware of evidence to support or refute the evolution of life during this period, but if Earth experienced late heavy bombardment at ca. 3.9 Ga, then refugia for life existed only beneath the surface or in space.

Carbocation reactions in sediments: The liquid reaction environment.

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The proportions of methylated naphthalenes in crude oils show relationships which are remarkably consistent in many different samples. Crude oils display constrained relations between the abundances of selected isomers, which are thought to be determined in the source rock before expulsion. For example, the ratios of three parameters, each based on the increase with maturity of stable isomers relative to less stable ones within a class of methylated naphthalenes, are linearly correlated to each other in crude oils. In contrast, in sediment extracts these relations are much less obvious. Similarly, the ratio of 1,3,6-TMN / 1,3,7-TMN shows a very narrow range of values in the oil set, but covers a much wider range in the sediments, although it appears to have an absolute minimum value.

To explain this behaviour of methylated naphthalenes it does not suffice to consider maturity and source effects. Therefore a new model is proposed involving a liquid reaction environment which is present in the source rock as an essential step in petroleum formation. The liquid reaction environment can be regarded as a liquid phase present in the source rock where it forms the medium for reactions that can take place between the many different organic compounds that are its constituents. It can be likened to a sedimentary reaction vessel, with its components forming both the solvent and the reactants. The reaction conditions within these liquids, of which temperature is the key factor, determine the composition of the petroleum before expulsion.

This model satisfactorily explains why the methylated naphthalenes display the relations as observed. Their distribution reflects the extent to which the system can take up input from the kerogen, and then redistribute the newly available methyl groups over the available naphthalene carbon skeletons. In contrast, when a sediment is extracted these compounds are mixed with methylated naphthalenes from other reaction environments present in the source rock, such as compounds adsorbed onto kerogen. This affects the total methylated naphthalenes distribution such that it no longer resembles that of a crude oil. The extent to which the liquid reaction environment has been established in the source rock can be gauged from the ratio of 1,3,6-TMN / 1,3,7-TMN. The closer this ratio in an extract is to that found in oils, the more the liquid reaction environment has contributed to the total extract.

Reactive transport in complex biogeochemical systems

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This contribution reviews recent progress and trends in reactive transport modeling (RTM) of biogeochemical systems, and discusses remaining challenges. Our premise is that a combination of process-oriented laboratory experiments, RTM and field validation is the most appropriate strategy to improve our understanding of the chemical dynamics of biogeochemical systems. Focus is on the use of RTM as intellectual support to interpret field-based data, design experimental studies and test implications of hypotheses. In this context, model development occurs iteratively, as new knowledge is continuously incorporated, and sensitivity analyses, rather than prediction, take central stage. Sensitivity analyses help identify the dynamical variables that dominate the behaviour of the system, but they also allow to compare and rank alternative model structures and process formulations. Powerful new approaches in RTM consist in combining traditional forward simulations with inverse, stochastic and adjoint modeling. Illustrative examples of RTM, applied to rivers, estuaries, sediments and aquifers, are discussed, with an emphasis on issues related to parameter identification, calibration, uncertainty and heterogeneity.

Present and past export of Southern Ocean deep water to the Pacific

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We present new Pb, Nd and Hf isotope time-series for two ferromanganese crusts, which have grown from central Pacific bottom water (D137-01, north of Samoa Passage, 7219 m water depth) and southern Pacific deep water (63KD, Tasman Basin, 1700 m water depth) over the past 38 and 23 Ma, respectively. Age models for both crusts were obtained by combining ¹⁰Be/⁹Be profiles and Co-flux modelling. Continuous time-series for Pb, Nd and Hf isotopes were measured at high precision using a Nu Plasma MC-ICPMS.

D137-01 is the deepest ferromanganese crust so far investigated for isotope time-series. Lead isotopes show a very different pattern from previously reported central Pacific records. Prior to ~ 17 Ma ²⁰⁶Pb/²⁰⁴Pb ratios are radiogenic (>18.80) and similar to "Atlantic" values whereas the present day ²⁰⁶Pb/²⁰⁴Pb ratio of 18.75 is intermediate between Southern Component Waters (≤18.85) and Pacific deep water (≤18.70). Two possible explanations for the observed trend are (i) a change in the isotopic composition of deep water exported from the Southern Ocean to the Pacific with time or (ii) a decrease in the flux of water masses from the Circum Antarctic Current to the Pacific Ocean. The likelihood of these interpretations can be tested by comparison with the second new record from the Tasman Basin. Overall there is a striking similarity of the two profiles and a remarkable agreement with general Pb isotope patterns in Southern Ocean crusts (Frank et al., 2002) and records from the Western Boundary Current in the South Pacific (Baker et al., 2001) over the past 14 Ma. Consequently, we suggest that the observed changes have been related to the export/composition of Southern Ocean water masses.

Final interpretations have to take into account the Nd and Hf isotope time-series from the same crusts as well. D137-01 shows relatively invariable ϵ_{Nd} and ϵ_{Hf} values over the past 38 Ma which are consistent with a two component mixture of Southern Ocean waters and Central Pacific bottom water. The picture for the Tasman Basin looks more complicated. Here we observe drastic changes (3 ϵ units) in Nd isotopes over the past 10 Ma which are accompanied by substantial changes in ϵ_{Hf} (2.5 ϵ units).

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Sr-Nd-Pb isotope constraints on magma genesis in the Sangihe Arc, North Indonesia

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The NNE-SSW trending Sangihe Arc in North Indonesia is currently in a process of complex collision with the Halmahera Arc, whereby the Molucca Sea Plate gradually disappears. Active volcanism accompanies westward subduction under the Sangihe Arc and eastward subduction under the Halmahera Arc. We carried out a regional Sr-Nd-Pb isotope and trace-element study along the entire 350-km Sangihe Arc, covering active volcanic centres in the chain of islands between Sulawesi and the Philippines and its continuation on the North arm of mainland Sulawesi.

Ranges in isotopic ratios of basalts and basaltic andesites (47.4-57.7 wt.% SiO₂) are modest, and do not appear to be influenced to a significant degree by contamination of arc crust. There is no clear along-arc trend. The ratios of ⁸⁷Sr/⁸⁶Sr (0.7037-0.7041), ¹⁴³Nd/¹⁴⁴Nd (0.5129-0.5130), ²⁰⁶Pb/²⁰⁴Pb (18.34-18.56), ²⁰⁷Pb/²⁰⁴Pb (15.56-15.64) and ²⁰⁸Pb/²⁰⁴Pb (38.30-38.64) tend to plot just outside local I-MORB type values, as defined by the Celebes Sea basement, which suggests a contribution of subducted sedimentary material. If the mantle component is assumed to be constant in the entire arc, the sedimentary component should be isotopically diverse. Mixing models are consistent with different Pacific Ocean type sediments as possible end-members. However, heterogeneity in the mantle component is plausible as well, given the complex tectonic history of the region.

Whereas there is a large overlap in Sr and Nd isotopic signatures of the Sangihe Arc and Halmahera Arc, mixing arrays in Pb isotope space do not coincide, which suggests involvement of different source components, despite the fact that both systems have the subducting Molucca Sea plate in common. We speculate that this may be related to an asymmetry in the arc-arc collision setting, as the Halmahera fore-arc has been forced to thrust under the Sangihe fore-arc, inducing favourable conditions for differences in the nature and amount of source components involved.

How to assess controls of Al in acidified soil solution

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Introduction

Based on research from the 1980's onward, the major sources of acid deposition have been identified, and measures for their reduction have been taken in many countries. However, questions on the effects on forest vitality (largely attributed to high levels of Al in soil solution), and on how we can effectively monitor/predict if and when the soil ecosystem will fully recover, still remain. An important recurrent question thereby, is what precisely controls Al levels in soil solution.

Conceptual reasoning

Basically, there are three different possible controls for the activity levels of solutes in the soil solution: a mineral solid phase (= thermodynamically fixed activity level), a mineral or organic exchange phase (variable activity level), and the vegetation (net input or net uptake). These controls can induce different states: that of true equilibrium, a non-equilibrium steady state, or a non-equilibrium transient situation. From theoretical considerations it can be argued that only two realistic steady-state end-situations can be reached:

1) Non-equilibrium dissolution of a primary mineral phase (in combination with the net flux from the vegetation); equilibrium of solution phase and exchange phases with a secondary mineral phase through fast precipitation. In this situation the activity level of Al in all phases except the primary mineral phase is the same, as fixed by the secondary mineral phase.

2) Non-equilibrium dissolution of a primary mineral phase (in combination with the net flux from the vegetation); non-equilibrium precipitation of a secondary mineral phase; equilibrium of the solution phase with the exchange phases. In this situation the combined kinetics, not the equilibrium with the exchange phase, determine the steady state activity in the solution phase.

Conclusion

Focus in soil acidification research is on dissolution kinetics and analysis of the soil solution's equilibrium state. For the second situation, however, these approaches are inadequate in predicting activity levels in soil solution, as precipitation kinetics and transport need to be considered as well.

Helium isotopic evidence for mantle reservoirs: a matter of melting?

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The large differences in helium isotopic systematics between mid-oceanic ridge basalts (MORB) and ocean island basalts (OIB) have traditionally been used as a primary constraint on the preservation of distinct mantle reservoirs over geological time. This appears at odds with the observations for whole mantle flow. Although mantle flow can be moderately sluggish, depending on the influence of the transition zone phase changes and the role of variable rheology, model calculations show that the mantle after Earth's formation should become reasonably well mixed at present day (e.g., Van Keken and Ballentine, 104, *J. Geophys. Res.*, 1999). Interestingly, the renewed interest in mantle mixing has led to a revival of ancient arguments for and against mantle layering, with no apparent resolution in sight. It is therefore worthwhile to explore alternatives that question whether we are reading the mantle signals correctly. For example, it has been suggested (Marc Spiegelman, pers. comm.) that the differences in MORB and OIB He isotopes could be solely due to mixing in the melt phase, where the larger percentage of melting of MORB would naturally lead to strong averaging of an OIB-like mantle signature. We have investigated this hypothesis by developing high resolution mixing models, based on our earlier work. This allows for quantitative predictions of the differences between OIB and MORB sampling of a heterogeneous mantle using a simple proxy for mantle melting that depends on the assumed size of melting region.

Surface chemistry of reactive mineral colloids

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The reactivity of mineral colloids in the environment is to a large extent determined by the surface chemistry of the mineral particles. The present challenge is to link the macroscopic behaviour, which determines the observations as done in the field with atomic level detail that from a fundamental perspective determines the microscopic reactivity. The combination of modern spectroscopic techniques like EXAFS, NMR, IR with quantum mechanical calculations leads to insight in the structure of species adsorbed at particular reactive surfaces. Protons, metal ions, oxyanions and natural organic matter interact at the surface of metal(hydr)oxides when present in the environment. Adsorption models are therefore needed which are based on molecular level detail and which can still handle the complexity of the environmental colloidal system. The CD-MUSIC model is a framework that can link the microscopic with the macroscopic. The (refined) MUSIC (MULTI Site Ion Complexation) model also estimates the proton affinity constants for the various reactive groups at the mineral surface, which is crucial for the basic variable charge behaviour of mineral particles. The CD stands for Charge Distribution. Inner-sphere surface complexes cannot be treated as point charges in variable charge adsorption models if one intends to use physically realistic surface species in the adsorption model. It has been shown that the charge distribution in the CD-MUSIC model determines the pH dependence of the adsorption, and that the charge distribution is linked to the structure of the adsorbed complex. The colloidal behaviour of mineral particles is also greatly affected by the charge/potential at the mineral/water interface. Adsorption of natural organic matter can have a large impact on the colloidal behaviour of the mineral particles. We have recently developed the LCD (Ligand and Charge Distribution) model that combines the NICA (Non Ideal Competitive Adsorption) model, which has been developed to describe competitive ion binding to natural organic matter, with the CD-MUSIC model to describe adsorption of natural organic matter on mineral particles. The model has so far been used to describe adsorption of some well-defined poly-carboxylic benzene molecules and FA adsorption on goethite. The model is in principle able to predict the interaction with both cat- and anions at the surface. An overview will be given of the various model concepts mentioned above in the light of the colloidal behaviour of mineral particles in the environment.

Graphite and its isotopic composition as a biomarker in highly metamorphosed Early Archean rocks

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The principal method for studying the earliest traces of life in the metamorphosed, oldest (>3.5 Ga) terrestrial rocks involves determination of isotopic composition of carbon, mainly prevailing as graphite. However, our results on rocks from the 3.8 Ga Isua supracrustal belt point to several complications using graphite as a biomarker and highlight the need for reassessment of some earlier biologic interpretations made on Isua rocks.

It is shown by stepped-combustion-mass spectroscopy experiments that the results obtained by single-step combustion techniques (sealed tube combustion, elemental analyser flash combustion) can be unreliable. The light isotope values in graphite deficient samples can in part or in total be derived from recent contamination. Furthermore, N, O and H found in carbonaceous material, which would point to a biogenic origin, are often related to recent contamination as well.

Several abiogenic processes can form graphite during metamorphism. Theoretical and experimental studies have shown that kinetic isotope fractionation associated with graphite-producing reactions may form graphite with a light 'biogenic' isotope signature. Kinetic effects may explain isotopically light graphite in some Isua rocks.

The potential of graphite as a biomarker has to be considered in geologic context involving reliable protolith interpretation and control of secondary metasomatic processes. Graphite in non-sedimentary rocks, regardless of its isotopic composition, has no biological significance. The original biologic interpretations in Isua rocks were made on carbonate rich deposits, but the recent recognition of these as metasomatic formations disqualifies them for providing information about life 3.8 Ga ago.

Isotopic constraints on the origin of Heinrich event precursors

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The origin of Heinrich events and the associated higher frequency 1-2kyr climate cyclicity are still not fully understood (Broecker and Hemming 2001). It has been clear for some time that the main phase of Heinrich events is characterised by the collapse of the Laurentide ice-sheet. However, the realisation that the 1-2 kyr cyclicity continues into the Holocene (Bond et al. 1997), in combination with Sr-Nd isotopic constraints on the variety of sources for Heinrich layer IRD, has led to the recognition that other ice-sheets must be involved. Information on the early stages of Heinrich events is obviously crucial to understanding their trigger and, perhaps, the ultimate mechanism for millennial climate change. Recently, Grousset et al. (2001) have suggested, on the basis of Sr-Nd isotopic data that, for H1 and H2, the collapse of the European ice-sheets occurred first and that only then was the collapse of the Laurentide sheet triggered. Here we present high resolution (1-200 yrs) Sr-Nd-Pb isotope data for bulk sediments from Heinrich events 2 and 4 at DSDP Hole 609 to test whether such a conclusion extends to other Heinrich events in other geographic locations.

Background glacial sediment at site 609 represents a mixture between three sources – North America, Iceland and Europe. The data for H4 at site 609 suggests that the source of the coarse fraction of the sediment immediately prior to H4 is the same, isotopically, as background glacial sediment. The first increases in IRD at the start of H4 correspond with a dramatic shift towards the North American source. For the early stages of H2, the data plot in the same region in Sr-Nd isotopic space as the Grousset et al. data for the same time period and also appear to suggest a European contribution. However, correlations between Sr and Pb isotopes reveal this to be impossible - indeed the early part of H2 contains about the same absolute amount of the European-derived end-member as background glacial sediments. The dramatic change at the start of H2 at site 609 is the dominance of Iceland – with up to 90% of the IRD being derived from this source. The dramatic increase in the Icelandic component early in H2 is consistent with the data of Bond et al. (1999) and suggests derivation of early H2 material from an area north of Iceland that is not, ultimately, the Fennoscandian ice-sheet.

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Triggered Star Formation and the Injection of Radioactivities into the Presolar Cloud

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Meteorite studies have revealed the presence of short-lived radioactivities in the early solar system. The current data suggests that the origin of at least some of the radioactivities requires contribution from recent nucleosynthesis at a stellar site. This sets a strict time limit on the time available for the formation of the solar system and has led to the formulation of the theory of the triggered origin of the solar system.

According to this scenario, the formation of the solar system was initiated when an interstellar shock wave originating from a nearby explosive stellar event impacted on a molecular cloud core. In addition to triggering the collapse of the molecular cloud core, the shock wave also deposited some of the freshly synthesized radioactivities into the collapsing system. The radioisotopes were then incorporated into the first solar system solids, in this manner leaving a record of the event in the meteoritic material.

The viability of the scenario can be investigated through numerical simulations studying the processes involved in the interaction between an interstellar shock wave and a molecular cloud core. The calculations suggest that star formation can be initiated in this manner and that an appreciable amount of shock wave material – approximately 10% - can be injected into the collapsing system by Rayleigh-Taylor instabilities. The calculations also suggest that temporal and spatial heterogeneities in the abundances of the radioactivities may have existed at the time of their arrival in the forming solar system.

Micro-scale Pb distribution and oxidation in a shooting range soil

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Deposition of shotgun bullets is the major source of lead contamination of soils near shooting ranges. The environmental impacts of shooting range soils contaminated with up to 30'000 ppm Pb has long been ignored, since metallic Pb(0) in shotgun bullets has been regarded highly immobile and inert. However, recent studies found that Pb bullets in soils develop corrosion coatings within a few years (Lin, 1996; Lin *et al.*, 1995). Some studies also reported elevated Pb concentrations in the subsoil at contaminated shooting ranges (Murray *et al.*, 1997) indicating a potential for Pb mobilization and transport into underlying aquifers. To clarify the mobility of Pb in shooting range soils, we are investigating the spatial distribution and chemical speciation of Pb and other elements in several shooting range soils on a centimeter to micrometer spatial scale.

Undisturbed soil samples were collected from various depths of a shooting range soil in Switzerland. After embedding the samples in resin, ~200 µm thick sections were prepared for micro X-ray fluorescence (µ-XRF), micro X-ray diffraction (µ-XRD), and micro X-ray absorption spectroscopic (µ-XANES) analyses. A preliminary elemental mapping was performed on a laboratory µ-XRF instrument (Eagle-II µProbe, EDAX) using a capillary optics producing a focussed X-ray spot of ~50 µm diameter. Selected areas were then analysed by µ-XRF, µ-XRD, and µ-XANES at beamline X26A of NSLS using a spot size of ~15 µm.

Elemental mapping of soil thin sections including fragments of shotgun bullets showed ~1 mm thick corrosion mantles around the metallic Pb. Analysis of selected areas by µ-XANES revealed that the corrosion mantle consists of a mixture of Pb(0) and Pb(II), while at greater distance from the bullets only Pb(II) was detected. The migration of Pb(II) away from the bullets into the soil matrix was clearly shown by µ-XRF elemental mapping. However, the magnitude of Pb spreading into the soil was rather low, suggesting that Pb is highly immobile in the soils studied.

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An active magmatic hydrothermal system at Copahue volcano, Argentina

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Copahue (Argentina) is an andesitic volcano with a crater lake and acid hot springs that feed the Rio Agrio river system. Primary glass inclusions in plagioclase and olivine have 1110-1670 ppm Cl, 90-400 ppm S and low water contents (0.4 - 1.5 percent). The hydrothermal fluids have S/Cl = 2, whereas the glass inclusions have S/Cl = 0.2, indicating preferential sulfur degassing. The hydrothermal fluids, with 6 % sulfate, are rich in rock-forming elements, with up to 2200 ppm Mg. The stable isotope composition of the spring waters ($\delta^{18}\text{O} = -2.1$ to $+3.6$ ‰; $\delta\text{D} = -49$ to -26 ‰) indicates that these fluids consist of up to 70% of volcanic brine and 30% glacial melt water. Dilution of the Rio Agrio produces values closer to local meteoric waters ($\delta^{18}\text{O} = -11$ ‰; $\delta\text{D} = -77$ ‰), whereas evaporation in closed ponds led to very heavy water (up to $\delta^{18}\text{O} = +12$ ‰). The $\delta^{34}\text{S}$ value of dissolved sulfate is $+14.2$ ‰, whereas the S^0 has values of -8.2 to -10.5 ‰. The isotopically heavy sulfate formed when SO_2 disproportionated into bisulfate and liquid native sulfur at about 300 °C.

The bulk-rock removal rate in the hydrothermal system through dissolution, calculated from river flux data and crater lake energy modelling, is on the order of 25,000 m³/yr. That void space is filled with a mixture of hydrothermal silica, liquid S^0 , and possibly minor anhydrite and Cu-sulfides. Stored liquid sulfur was ejected as pyroclastic sulfur during the 1995/2000 eruptions. Estimated annual metal fluxes for Copahue are 10 tonnes Zn, 5 tonnes Pb, 3 tonnes Ni, 7 tonnes Cr and 15 tonnes As. Copper tends to be highly depleted in these fluids, suggesting precipitation of Cu minerals in the underlying hydrothermal system. The isotopic signature of the magmatic SO_2 is estimated at $\sim +7$ ‰, which is a source signature with superposed effects of shallow degassing. Lead isotope and ¹²⁹I data from the fluids indicate the presence of subducted components in the Copahue magmas.

Petrology and Geochemistry of Çamlidere Volcanic Rocks, Central Anatolia, Turkey: Preliminary Results

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The Galatean Volcanic Province is a large volcanic zone developing as a result of Miocene continental rifting, at the south of the North Anatolian Fault Zone, northwestern Anatolia, Turkey. The Çamlidere volcanic rocks are located at the northern central parts of this province and we herein report the preliminary results on their petrology and geochemistry whose characteristics are poorly known. We observe that domes, lava flows, pyroclastic flow and fall deposits are the eruptive products of Çamlidere volcanic complex. Pyroxene, amphibole, plagioclase, biotite and oxides are dominant phenocrysts in volcanic rocks and quartz is an accessory phenocryst in dacites and rhyolites. Çamlidere volcanic rocks exhibit a wide range of SiO_2 content (49 to 76 wt%) and are composed of trachybasalt, basaltic trachyandesite, trachyandesite, trachyte, andesite, dacite and rhyolite. Pyroclastics are predominantly rhyolitic in composition. Total alkali-silica diagram shows alkaline and calcalkaline character. The variation diagrams of SiO_2 versus major elements are consistent with fractional crystallisation process.

Temperature-dependent oxygen isotope fractionation factor for dolomite: Constraints based on bacterial culture experiments

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The origin of dolomite has long been an area of controversy, as it has proven extremely difficult to precipitate it in the laboratory under Earth's surface conditions. As a result, the experimental temperature-dependent dolomite-water oxygen isotope fractionation factor has remained undefined. Different approaches were taken, however, to establish the relationship among $\delta^{18}\text{O}_{\text{dolomite}}$, $\delta^{18}\text{O}_{\text{water}}$ and precipitation temperature. For example, extrapolations from high temperature experiments or indirect measurements from Holocene examples of co-existing calcite and dolomite, without any control on the time of precipitation, were used. These extrapolations and assumptions led to inconsistent results and the stable isotope geochemistry of dolomite continued to be one of the most enigmatic and complex in sedimentary geochemistry.

A new line of research indicates that dolomite precipitates in the laboratory at low temperatures mediated by microbial metabolism under anoxic conditions (Vasconcelos et al., 1995; Warthmann et al., 2000). The results of our microbial experiments, using specific strains of sulfate-reducing bacteria, show that, at 25 and 30 °C, a mixture of high Mg-calcite and Ca-dolomite formed, whereas, at 40 and 45 °C, pure stoichiometric dolomite was obtained. Using a dolomite-phosphoric acid fractionation factor of 1.0093 for the reaction temperature of 90 °C (Rosenbaum and Sheppard, 1986), the dolomite-water fractionation is described by the equation: $1000\ln\alpha = 2.734 * 10^6 T^{-2} + 0.26$. This equation indicates that, at equilibrium, the oxygen isotope composition of dolomite would be approximately 2.2 ‰ more positive than that of the co-existing calcite. Based on this equation, we are now able to better evaluate the environmental or diagenetic conditions under which ancient dolomites precipitated. Further, we propose to reinterpret previously reported isotope fractionation data, which were used to assess the mechanism(s) of dolomite formation.

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Fluoride Sorption and Associated Al Release in Iron Oxide Rich Soils

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Introduction. Anion-soil interactions play an important role in determining soil weathering, nutrient availability, and contaminant fate and transport. Sorption of anions, particularly fluoride (F^-), is often a precursor to Al dissolution: the electronegative F^- replaces $-\text{OH}/\text{H}_2\text{O}$ groups bound to surficial Al atoms (ligand exchange), loosens other Al-OH bonds and facilitates the dissolution of Al from the surface [1-2]. Our understanding of anion interactions in soils of temperate regions is relatively well advanced. In comparison, our knowledge of anion behaviour in variable charged soils, such as the prominent iron oxide rich soil orders (Ultisols and Oxisols), is limited.

Goals. This study is aimed at understanding F^- sorption and related Al release in Ultisols as a function of soil depth, composition and physical-chemical properties and evaluating potential mechanisms of fluoride-surface interactions. This study also addresses a related question: Is the extent of fluoride-facilitated Al release a useful measure of soil susceptibility to ligand (anion) promoted dissolution?

Methods. A total of ten samples representing A, B and BC horizons of a Georgeville soil and A, E, and B horizons of an Appling soil were obtained from freshly dug pits in Durham County, NC, USA. Following extensive characterization of the soils, fluoride sorption was measured in batch experiments over a wide aqueous F^- concentration range (0-15 mM) at soil pH and at an initial pH of 3.5. The Langmuir equation was used to derive the maximum extent of fluoride sorption (F_{max}) under each pH condition. Al and OH-release was monitored in experiments conducted at soil pH.

Findings. We find that fluoride sorption is strongly correlated with soil Fe and Al oxide content, anion and cation exchange capacities, and maximum phosphate sorption capacity. Although fluoride complexation to surficial Fe and Al ions is the dominant sorption mechanism, we find indirect evidence that implies fluoride precipitation in patches. For the Appling series, we find that Al release to soil solution is proportional to the extent of fluoride sorption and soil Al and Fe content. However, the Georgeville series exhibit low Al release despite possessing a high capacity for fluoride sorption and a high Al content. In this case, it is likely that the soil mineralogy protects against Al dissolution and/or fluoride sorption to surficial Fe is preferred over sorption to surficial Al ions. Measures of fluoride facilitated Al release may be a useful surrogate for soil susceptibility to ligand promoted dissolution.

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Millennial scale variability records in the western Subtropical Atlantic Ocean

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We present detailed results obtained from ODP Leg 172 Sites 1060 and 1056, from the Black Bahamas Outer Ridge (74°W, 31°N, 3500 and 76°W, 32°N 2200 meters water depth respectively) covering the last Glacial/ Interglacial cycle. These sites are at present under the influence of the Gulf Stream current and Deep Western Boundary Current (within the Lower NADW and Upper NADW respectively). These locations are therefore of key importance for understanding both meridional heat transfer and thermohaline circulation variability. The history of these processes is of particular interest in the context of millennial scale climatic variations. The high sedimentation rate (30 cm /kyr on average) at Site 1060 enables us to compare this new marine data set to the Greenland ice core in great detail over the interval covering the last glacial, when the amplitude of the millennial scale climatic variability was maximal.

To investigate the deep-water conditions we use benthic oxygen and carbon isotopes at the highest possible time resolution. To study the surface hydrological variability, comprehensive planktonic foraminifera fauna analysis has been carried out on both cores and is used to reconstruct the sea surface temperatures (SIMMAX). We have determined the lithic content of the sediment in the >90 µm fraction size and analysed the planktonic stable isotopes when possible.

Our results for site 1060 show that as far south as 30°N, subpolar planktonic foraminifera species (*N. pachyderma dextral*) can still trace the northern hemisphere cooling, that sea surface temperatures changes match the temperature fluctuations recorded in Greenland and that iceberg signals can be detected even during stadial periods. Located right on the path of the present Gulf Stream Current, Site 1056 shows both a different pattern of surface SST's and overall warmer values, reaching 28°C in summer during the interstadial 8. This new record may indicate a more continuous activity of the warm surface current during Glacial times than previously thought. However cold events can still be recognised, mainly in the winter temperature and are attributed to the cold Heinrich events.

Constraining the timing of magmatic evolution in the Youngest Toba Tuff rhyolite through dating of zoning in allanite

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Dating of zoned crystals serves as an absolute means of quantifying the rates and timing of chemical change in the magma reservoir as well as correlating zoning between crystals. We present the first quantification of the age-compositional relations recorded by the compositional zoning of phenocrysts. By keying *in situ* ion microprobe ages to the chemical variations in allanite, a Th and LREE-rich epidote mineral, we resolve the timescales of magmatic evolution associated with the compositionally diverse (69-75 wt.% SiO₂) rhyolite of the 75 ka Youngest Toba Tuff (YTT). From the magnitude of ²³⁸U-²³⁰Th disequilibrium, most YTT allanite are ≤150 ka with most rim ages identical to that of eruption. Allanites from a fine-grained crystal-mush inclusion yield a similar age distribution but are distinct in size and composition from allanite in their host, suggesting that allanites within the host pumice are not simply derived from disaggregation of inclusions. Moreover, core-to-rim age distributions in single crystals suggest that the allanites are the product of crystal growth and magmatic evolution over 10's of ky. Compositional zoning of the YTT allanites occurs on a scale of 10's of microns and is defined by changes in both major, minor, and trace elements, with gross core-to-rim trends of decreasing LREE, MgO, and La/Nd, and increasing MREE, MnO/MgO, and ThO₂. The trends can be simply ascribed to growth from a melt evolving via crystal-melt fractionation rather than being due to re-equilibration or kinetic effects associated with allanite growth. However, some grains display opposite zoning trends and/or contain resorbed and evolved cores. Furthermore, zoning ranges from monotonic to oscillatory with distinctive resorption surfaces, and compositions of allanites from the most- and least-evolved YTT pumices overlap, suggesting complex crystal and magma histories. When considered together, the coupled time-composition relations of the zoning between different allanites are sufficiently disparate so that no absolute correlation exists between composition and age. This in turn suggests that individual YTT allanites record complex growth/magmatic histories and/or have "seen" compositionally diverse melts that persisted for 10's of ky prior to eruption of this voluminous rhyolite. Evidently, reconstructions of magmatic evolution from correlations of compositional zones between associated allanites, and possibly other phases, should be approached with caution.

Experimental evidence of the role of liquid immiscibility in evolution of granitic pegmatites and Li-F granites

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Recent studies of melt and fluid inclusions in pegmatites of Ehrenfriedersdorf, Germany (Thomas et al., 2000), demonstrated extreme enrichment of the evolved granitic melts in B, F and P. Other examples of evolved granitic systems show large variations in absolute concentrations and relative proportions of the volatiles and fluxes. For instance, quartz-hosted melt inclusions from the Malkhan tourmaline-rich pegmatites in Russia show extreme enrichment in B (up to 6.7 wt% B₂O₃), but low F contents (about 0.1 wt%). High B contents, around 2 wt%, were also found in melt inclusions from highly evolved rocks of the Orlovka massif (Russia), which is a classical example of strongly differentiated intrusion of Li-F granites. Inclusions in the Orlovka contain up to 1.8 wt% F and differ from those in Malhan not only in F, but in proportions of major oxide components as well.

In all the three cases represented by the Orlovka, Malkhan and Ehrenfriedersdorf, we find in melt inclusions evidence of three distinct coexisting fluids operating at final stages of magmatic evolution. They are: (1) aluminosilicate melt of granitic composition; (2) a second melt, composed mostly of borates, or fluorides, or both; and (3) H₂O-CO₂ low-density fluid with variable amounts of NaCl, H₃BO₃ and other solutes. The coexistence of three immiscible fluid phases was recently confirmed by hydrothermal experiments in diamond cells and rapid-quench pressure vessels using a synthetic granitic composition spiked with B, P and F (Veksler et al., 2002). Our results are in good agreement with previous studies of liquid immiscibility between aluminosilicate and fluoride (cryolitic) melts (Gramenitskiy and Schekina 1994). In on-going experiments we find evidence of silicate-borate liquid immiscibility in granitic systems doped with Li₂B₄O₇. Thus, liquid immiscibility appears to cover a broad range of bulk compositions from B-rich to F-rich melts and is likely to be common in the highly evolved granitic systems. It should strongly affect the behaviour of trace elements and major components and may be responsible for a number of characteristic chemical features of pegmatites and Li-F granites.

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Numerical modelling of competitive nucleation pathways

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The development of numerical models for the description of nucleation processes is an important step to model the sequence of phase reactions that takes place in sediments during the early diagenetic transformations, in particular, when reaction-speciation codes are employed.

In this work a numerical model based in nucleation and growth algorithms has been designed to compute the temporal sequences of precipitation and phase transformation kinetics in metastable solutions of polymorphic or hydrated substances. This model has been designed for the treatment of kinetic data, both for nucleation and crystal growth following experimental results of various macroscopic techniques, sensitives to some macroscopic property variable related to mass crystallized on time or given a density population distribution in crystal size (i.e. calorimetry, dynamic-XRD, etc.). It allows, furthermore, for the analysis of the influence of nucleation algorithms based on different thermodynamic considerations (referring mainly to the surface tension and the grain size distribution) of the parameters involved in the process.

The main part of the program consists of a sequence of algorithms that describe the crystalline growth kinetics by applying the balance equations to the usual expressions for the growth and supersaturation rate.

The initial growth conditions are made dependent on a subroutine containing nucleation algorithms that includes several thermodynamic approximations to the metastable interval, mainly connected with the estimation of the free Gibbs surface energy [1].

Fits to experimental values are obtained by optimizing the adjustable parameters introduced in the nucleation equations by the Marquardt algorithm.

The use of an analytical optimization model, alongside the program, facilitates the search for a better compromise between the kinetic nucleation parameters and said macroscopic effects experimentally observed both in one single phase precipitation systems as well as polymorphic or hydrated substances, in which the sequential precipitation of different phases takes place.

Since it is possible to use nucleation algorithms based on different thermodynamic considerations, the model is at the same time useful in the discussion of the viability of different nucleation mechanisms in natural systems.

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This study was supported by Spanish MCYT BTE2000-0877 project.

An enigmatic salinity source in the Mediterranean coastal aquifer and Gaza Strip: Utilization of isotopic (B, Sr, O) constraints for searching the sources of groundwater contamination

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The Scope of the Problem

The southern Mediterranean coastal aquifer is suffering from a severe water quality crisis that endangers future exploitation for a population of over one million living in the coastal area of Israel and the Gaza Strip. The most conspicuous phenomena are the ongoing salinization (>2000 mgCl/l), boron (<4 mg/l), and nitrate pollution (<460 mg/l).

Results and Discussion

In the framework of the European research project BOREMED, co-financed by the European Community, geochemical and isotopic (B, Sr, O) investigation of groundwater was conducted in the southern coastal aquifer of Israel and Gaza Strip. It reveals three major water types: (1) Eastern saline groundwater with Na/Cl >1, high B/Cl (9×10^{-3}), and $\delta^{11}\text{B}$ values (48‰) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70802 to 0.70819; (2) Sea-water intrusion with Na/Cl <0.86, low B/Cl ($<8 \times 10^{-4}$) and high $\delta^{11}\text{B}$ values (>40‰); and (3) Nitrate-rich groundwater within the Gaza Strip with high Ca content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70815 to 0.70875.

We use the geochemical variations to reconstruct the principle flow paths. The eastern saline groundwater component is the major source of salinity in a large area of the aquifer. Over-exploitation in the Gaza Strip resulted in declining water levels, which resulted in intensification of east-west flow. Nitrification process enhances dissolution of the carbonate matrix of the calcareous aquifer, as evident by linear relationships between NO_3 , Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

The Boron Source Enigma

The Na-SO₄-HCO₃ composition of the eastern saline groundwater can be interpreted by several possible geochemical mechanisms (e.g., gypsum and carbonate dissolution coupled with base-exchange reactions, silicate hydrolysis such as alteration of albite into kaolinite, flushing of seawater intrusion by freshwater). The enrichment of both elemental boron and $\delta^{11}\text{B}$ values rules out, however, all of these possibilities. The origin of the eastern saline groundwater, which is the major source of salinization in the Gaza Strip, has yet to be resolved.

Laser-based oxygen isotope analysis of biogenic silica

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Oxygen isotope compositions of biogenic silica (SiO₂.nH₂O) provide a powerful paleoenvironmental proxy, particularly for regions where biogenic carbonate is rare or absent such as fresh water lakes, high-latitude oceanic regions, and the deep sea below the carbonate compensation depth. However, measurements of the O isotope composition of biogenic silica are complicated as it may contain as much as 13 weight % water, much of which is exchangeable. To obtain accurate estimates of the original O isotope composition it has been necessary to use fairly complex extraction procedures that avoid the exchangeable oxygen, or where controlled isotopic exchange approaches estimated original compositions for this component. Methods used either require relatively large amounts of sample (tens of mg) and/or are questionable for cases where it is difficult to estimate the original isotopic composition of exchangeable oxygen such as for fresh-water systems. To overcome these analytical problems, a method has been developed that employs a 30 W CO₂-laser to spontaneously heat and melt the biogenic silica in a vacuum, followed by fluorination of the residual melt bead. Initial rapid heating avoids exchange between released water vapors and the Si-bonded oxygen, as the vapors are condensed in a trap cooled with liquid nitrogen. The melted sample beads are then transferred to a new Pt sample holder for oxygen extraction using the CO₂-laser and ultrapure F₂ as reagent. Use of a distinct sample holder for melting eliminates cross-contamination that may occur through vaporization during melting and condensation of the vapors on the sample holders of a common sample chamber.

Tests on several 1 to 3 mg-sized quartz standards and samples of biogenic silica from sponge spicules indicate that vaporization during melting is limited and has no effect on the O isotope composition of the SiO₂. Repeated measurements are precise to within 0.2 permil. For sponge spicules from fresh waters (Lake Baikal, Biwa Lake) and the Caribbean Sea, for which the temperature and isotopic composition of water are known or can be estimated with reasonable certainty, temperatures calculated are in good agreement with actual temperatures. However, for other species of sponge spicules from the White Sea and the Weddell Sea, the agreement is poor, suggesting species-specific fractionation, isotopic exchange of the silica with pore fluids, or poor estimates of actual conditions. Experiments using cultured species of sponge spicules are in progress to place further constraints on these possibilities.

Search for Q: single grain Xe isotope analyses of graphitic residue from Yilmia (EL6)

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The nature of phase Q, the carrier of one of the major noble gas component in the Solar System [1] remains uncertain. All attempts to isolate it by physical methods have failed [1-3]. Recently we have shown that being carbonaceous in nature, the carrier is nonetheless distinct from the majority of carbon matter present in meteorites in its chemical properties. In particular it is not graphitised under reducing conditions in enstatite chondrite parent bodies: significantly different combustion temperatures for Q and majority of graphitic carbon in Yilmia (EL6) was observed [4]. However even in this, seemingly favourable case, Q cannot be physically separated from the majority of graphitic material present in the meteorite. This presumably indicates that Q is somehow closely physically associated with graphitic grains.

In order to understand how the different phases are related to each other we decided to analyse single carbonaceous grains from Yilmia HF-HCl residue for Xe using the high sensitivity RELAX instrument [5]. Most of the grains were analysed using Raman spectroscopy in order to identify carbonaceous grains and characterise their structural features.

Only 20 out of more than 200 grains analysed yielded Xe above (factor of 2-4) the procedural blank level ($1-1.5 \times 10^{-16}$ cc ^{132}Xe). The concentration of Xe in the grain with highest measured yield is about 10^{-7} cc/g which is almost two orders of magnitude less than expected for Q. Moreover, the concentration of Xe measured in all the grains we analysed is less than 10^{-9} cc/g – again almost two orders of magnitude less than in the bulk sample.

The obtained results clearly indicate that Q is not equally associated with all carbon grains. The association is not adsorption of gas on the grains nor “adsorption” of small Q-grains on larger graphite grains. Thus, we have to conclude that the relationship between Q and other carbonaceous grains is quite specifically related to the, so far unknown, properties of Q, so that only some rare particular graphitic grains are involved in the relationship.

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^{10}Be measurements on Neolithic and Paleolithic flint tools from Israel

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The analysis of the ^{10}Be content of prehistoric flint tools could help in the understanding of cultural and technological issues connected to the mining of chert in the Neolithic and Paleolithic. Since the quality of the raw material (chert) is important in flint knapping, the study of the development of mining is of much interest. The determination of the presence of the cosmogenic isotope ^{10}Be (half-life = 1.5 million years) in flint samples can be used to address this problem. Radioactive ^{10}Be is a cosmogenic nuclide that is produced *in situ* in mineral crystals. The presence of ^{10}Be in prehistoric flint tools would indicate the use of surface materials as opposed to mined materials. In a control study of mined flint in Ramat Tamar, a Neolithic mining site in the Negev desert (Israel), the comparison of ancient tools, buried and exposed chert nodules allowed us to confirm this hypothesis. The ^{10}Be concentration, measured by accelerator mass spectrometry (AMS), shows that the buried nodules and the flint worked fragments have much less ^{10}Be than flints exposed on the surface. The average amount of ^{10}Be per gram of initial flint for tools and buried nodules is about 0.2×10^6 ^{10}Be atoms per gram of initial material. This is consistent with the flint tools having been formed from mined raw materials. The exposed flints display a wide variation: $1.7-4.0 \times 10^6$ ^{10}Be atoms/g of initial material, indicating maybe different exposure and erosion histories at the surface. One exposed flint overlaps completely with unexposed nodules; it was presumably exposed for a relatively short period. The same approach is being applied to archaeological samples coming from two Paleolithic caves in the north of Israel. The novelty of this application of ^{10}Be detection and the important cultural aspects of tool fabrication, make this research fascinating. Hopefully it will contribute to our understanding of a part of human history where scientific data are rare and difficult to obtain.

The Lu-Hf-Nd isotopic signature of subducting pelagic sediments

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The anomalous Lu-Hf-Nd isotopic signature of some pelagic sediments (high Lu/Hf; Hf-Nd isotopic compositions that plot above the terrestrial array) give them the potential to be a useful tracer as they pass through the subduction zone and into the mantle. The limitation in their utility as a tracer is that we do not know in any quantitative way the isotopic composition of the global flux of subducting sediments. Therefore, in this study, we are examining a global set of subducting sediments in order to constrain how widespread this signature is, what sediments contribute to this signature, how it varies from trench to trench, and ultimately what causes elevated Lu/Hf and unusual Hf-Nd isotopic compositions.

We have examined two DSDP sites to date: 183 and 595/6, located outboard of the Aleutian and Tonga trenches, respectively. The Aleutian section is dominated by diatomaceous clay and terrigenous turbidite sequences that constitute > 90% of the 516 m thick section. In total, this section has typical crustal Lu/Hf ratios ($^{176}\text{Lu}/^{177}\text{Hf} = 0.008\text{--}0.022$) and has Hf-Nd isotopic compositions that lie within the Hf-Nd array. However, the 1-4 meter hydrothermal sedimentary unit at the base of the section has highly elevated Lu/Hf ($^{176}\text{Lu}/^{177}\text{Hf} = 0.078$) and has a Hf-Nd isotopic composition that plots above the Hf-Nd array and provides evidence for the origin of anomalous Lu-Hf-Nd signatures. This unit has very high REE concentrations (Nd~200 ppm), but average Hf (4 ppm). The anomalous Lu-Hf-Nd signatures appear to be produced by a decoupling of the source of Hf and Nd in these sediments: Nd is derived from scavenging of REEs from seawater and is ultimately of continental origin and Hf is dominated by hydrothermal inputs with a mantle isotopic signature. Although Hf in these sediments has been the focus because of its radiogenic nature, it appears that REE inputs also have an important influence on the development of the anomalous Hf-Nd signature and high Lu/Hf ratios.

The Tonga section, in contrast, is characterised by a very slow accumulation rate and is dominated by authigenic phases and red/brown clays. Preliminary data indicate that this section in total is characterised by very high Lu/Hf ratios ($^{176}\text{Lu}/^{177}\text{Hf} = 0.040\text{--}0.185$; avg. = 0.107) and radiogenic Hf, in contrast to the more crustal character of the Aleutian section. Although the sediment column here is thin (~70 m), it nonetheless represents an important flux of a distinctively anomalous Lu-Hf-Nd signature into the subduction zone and mantle.

Constraints on basalt erosion from Li isotopes and U-series nuclides measured in Iceland rivers

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Weathering of Ca-Mg silicates is considered as a significant sink of atmospheric CO₂, and the importance of basalt weathering, particularly on the seafloor and in volcanic islands, has been recently demonstrated (Louvat and Allègre, 1998; Brady et Gislason, 1997). Nevertheless, because of the lack of convenient proxies, no consensus exists on the paleovariations and controlling factors of silicate weathering rates. U-series measured for the weathering products carried by rivers can be linked to both the age and the degree of chemical erosion at the scale of a watershed (Vigier et al., 2001). Li isotope ratios measured in rivers may also reflect the intensity of silicate weathering (Huh et al., 2001).

About 30 rivers have been sampled in Iceland in 2001. Despite low-levels of trace elements for the dissolved phases of these rivers (U and Li contents range from 0.5 to 75ng.l⁻¹ and from 0.03 and 4.5µg.l⁻¹ respectively), recent developments with the Multicollection ICP-MS 'Nu-Instrument' allow ($^{234}\text{U}/^{238}\text{U}$) and $\delta^6\text{Li}$ to be analysed precisely.

First results show significant variations of ($^{234}\text{U}/^{238}\text{U}$) (from 1.65 to 1.07) suggesting that the weathering of *silicates* can yield a large range of values, down to ~1 (secular equilibrium). $\delta^6\text{Li}$ for dissolved phases of these rivers range between -16.8‰ and -23.3‰, suggesting that $^6\text{Li}/^7\text{Li}$ ratios fractionate during weathering of the source basalts ($\delta^6\text{Li}_{\text{MORB}} \sim -4.5\%$). Highest ($^{234}\text{U}/^{238}\text{U}$) and lowest $\delta^6\text{Li}$ have been found for rivers characterised by low U and Li contents, draining old basalts (>0.7my) in areas with low weathering rates. By contrast, the lowest ($^{234}\text{U}/^{238}\text{U}$) corresponds to the highest $\delta^6\text{Li}$ and the highest U content, in a SW area (Holsa River), which has previously shown to have the largest weathering rates of Icelandic basins (Gislason et al., 1996).

If these results are confirmed by future data, it would strongly support the hypothesis that both U and Li isotopes can reflect the degree of silicate weathering. The associated analyses of Th and Ra isotopes for the same rivers should also allow us to estimate the role of the last glaciation on chemical weathering of silicates in this area.

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Where is geochronology going? Alteration and mineral mixtures

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Ore geologists owe their living to water released by crystallizing granitoids. This fluid phase shows enhanced activities of aggressive anions, and wall rocks. Do contact aureoles teach us universally applicable principles?

"Alteration" of a mineral is its modification by a different process from its formation. Metamorphic processes are a subfamily of alteration; the connection becomes even more obvious if one considers that the modern consensus on metamorphism stresses the great importance of fluids.

The perception of "minerals" has been greatly modified by electron beam analyses. TEM and EMP have shown a whole new world in which minerals are no longer as simple as was believed 50 years ago: inclusions, inter/overgrowths, replacements and relics are now considered to be ubiquitous. How can geochronologists adapt to a changing paradigm, according to which most carrier phases of the isotopes used for dating are mixtures?

Real progress in zircon dating was achieved when cathodoluminescence images were coupled to sensitive spot analyses. Petrographic and textural criteria were used to guide the interpretation of isotope analyses. Accretion of hydrothermal or metamorphic rims was shown to be one of the principal mechanisms causing discordance. This ended a 40-year-old dispute on the role of diffusive losses: it is now certain that diffusion is a very slow process which always will be overrun by recrystallization whenever water is available.

After the door was opened, other minerals also benefitted from detailed petrographic characterizations. A common pattern emerged: monazite can record younger ages at the core of a crystal than at the rim - matching with recrystallization textures; muscovites give different laser Ar-Ar ages as a function of shear-induced recrystallization or of their Si content, a monitor of their differential recrystallization under changing PTAX conditions.

Accepting the petrographic evidence that many minerals are polygenic mixtures rather than homogeneous gems must open up new paradigms for isotope geologists. If each mineral generation can retain the elemental and isotopic record of its formation, it becomes necessary to discriminate the signature of each. When laser ICP or laser Ar-Ar analyses are not sufficiently precise, it is possible to exploit an alternative technique. Stepwise release experiments contain chemical information, e.g. the Th/U and Pb/U, or Ca/K and Cl/K element ratios given by Pb and Ar isotopes, respectively. This must be tied to electron microprobe analyses so as to firmly identify the isotope reservoirs and assign each of them an individual age.

Example: Pb/Pb and Cl/Ar ratios in contact halo K-fsp (Sardinia) correlate with deuteric replacement textures.

Re-calibration of surface complexation models for magnesite and dolomite using Brown valence theory and a genetic algorithm

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The CD-MUSIC (Charge Distribution MULTIsite Complexation) model offers a novel theoretical framework to study surface complexation on oxide minerals [1]. The model reconciles the bulk mineral crystallography with chemical and thermodynamic notions traditionally invoked by earlier models.

The first step in exploring the relevance of multi-site complexation to carbonate minerals is to estimate a new set of surface parameters derived from crystal chemistry and Brown-valence theory in order to re-calibrate existing models of surface complexation.

We estimated the density and residual charges of different reactive surface sites on the (104) plane of magnesite and dolomite according to the protocol applied to oxides [2]. These parameters were used to reformulate an earlier conceptual model of surface complexation for magnesite and dolomite in which integer rather than fractional residual charges were assigned to the surface sites [3,4].

Re-calibration of the surface complexation models was carried out by fitting values of the intrinsic complexation constants using published data of surface charge [3,4]. To this end, an in-house computer code was used. The code incorporates a genetic algorithm as a novel stochastic search and optimization technique. The intrinsic constants we obtain are similar to those reported in previous studies [3,4] and allow the simulation of the electrokinetic properties of both minerals under varying conditions of pH, ΣCO_2 and total metal concentration

The implications of our results for modeling multi-site complexation at the mineral-water interface of Ca-Mg rhombohedral carbonates will be discussed.

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Kinetic study of bio-barite preservation in deep-sea sediments

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Relationships between barite (BaSO₄) microcrystals production in the water column (bio-barite) and ocean productivity are now clearly established, although formation mechanisms are still poorly understood. As such quantitative information might be preserved in sedimentary records, barium (or more precisely bio-barite) has been proposed as a proxy to reconstruct paleoproductivity (Dymond et al., 1992; François *et al.*, 1995). Recently, Robin *et al.* (submitted) proposed a new method for quantifying directly biobarite concentrations in deep-sea sediments that allows low level detections. Additional studies aimed at validating the use of bio-barite as a proxy are still needed. As an example, the preservation of biobarite within sediments in relationship with pore water and sediment compositions has to be better understood.

In this work, we investigate sediment reactivity with respect to pore-water barium concentrations. As a first attempt, we utilize bulk sediments from the North Tropical Atlantic Ocean (EUMELI IV cruise, 3104 m water depth) and stirred micro-reactors. Experiments are designed to extract apparent solubility and dissolution/precipitation reaction rates. Preliminary solubility value for bulk sediments supports the hypothesis of a control of pore water barium concentrations by nearly pure barite precipitation. This result will be compared to that obtained with chemically separated bio-barite (van Beek and Reyss, 2001).

Geomicrobial Mechanisms of Carbonate Precipitation: Novel Insights from Laminated Structures

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Carbonates, including CaMg(CO₃)₂ and CaCO₃, are common features in sedimentary systems. Recently, several models for dolomite (Vasconcelos and McKenzie 1995) and aragonite (Reid et al. 2000) formation have been postulated.

Laminated sedimentary biofilms (e.g., microbial mats) are structures in which microbes live in close proximity, resulting in tight cycling of major elements (C, N, S, etc.). As with all elements, C cycling requires additional redox species to function: For example, electron donor for C fixation can be O (H₂O) or S (HS⁻, S₂O₃²⁻, etc.) and respiration of organic C is facilitated by O₂ or SO₄²⁻ (SO₃²⁻, S₂O₃²⁻, etc.). The C cycle is primarily an energy-transfer mechanism, in which reductive and oxidative processes are balanced. However, decoupling of these processes in time and/or space may result in permanent biogenic signatures: When respiration prevails, carbonates can be formed as a permanent signature.

We observed in various laminated sediment systems (Mexico, Bahamas, and Brazil) that a simple balance between oxygenic photosynthesis and aerobic respiration does not explain precipitation. Instead, S cycling needs to be considered: Spatial and temporal decoupling of SO₄²⁻ reduction and HS⁻ oxidation and metabolic diversity of organisms involved in S cycling are fundamental phenomena that determine whether precipitation or dissolution occurs. The laminated organization of populations, processes and products makes such contemporary structures very useful in understanding mechanisms of carbonate precipitation.

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Noble gases in chondrules and metal-sulfide rims of primitive chondrites - Clues on chondrule formation.

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Introduction

Chondrules in ordinary chondrites are often surrounded by metal-sulfide (MS) rims, which were possibly formed together with chondrules. Part of the MS rims were formed by expulsion of MS-droplets from molten chondrules and subsequent crystallisation on chondrule surfaces [Rambaldi and Wasson 1981, Alexander et al. 1889, Connolly et al. 2001]. Our noble gas study on trapped Ne and Ar in MS rims and chondrules of Bishunpur (LL3.1), Krymka (LL3.1), and Semarkona (LL3.0) supports this scenario and suggests a fractionation of the Ar-carrier phase Q and the Ne-carrier phase HL during chondrule formation.

Results

Most of the MS rims show high $^{36}\text{Ar}_{\text{tr}}$ but lower $^{20}\text{Ne}_{\text{tr}}$ than the surrounding fine-grained material, resulting in high $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{tr}}$ (Fig. 1). In contrast, several Semarkona and Bishunpur chondrules show very low $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{tr}}$ ratios, indicating preferential depletion of $^{36}\text{Ar}_{\text{tr}}$. We infer that during chondrule formation the $^{36}\text{Ar}_{\text{tr}}$ -carrier phase Q partitioned preferentially into the liquid metal phase, which was subsequently expelled from the chondrule and formed the rim. The residual silicate melt, which is now present as the chondrule interior, shows a corresponding deficiency in $^{36}\text{Ar}_{\text{tr}}$.

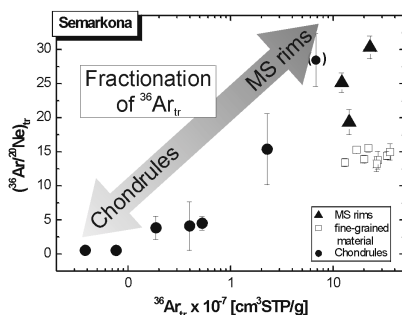


Fig. 1: $(^{36}\text{Ar}/^{20}\text{Ne})_{\text{tr}}$ vs. $^{36}\text{Ar}_{\text{tr}}$ of MS rims, chondrules and fine-grained material of Semarkona as an example. Brackets indicate contaminated samples. Errors

Conclusions

The trapped noble gas signatures of MS rims around chondrules and chondrule interiors support rim formation by expulsion of MS from chondrules during melting. The affinity of the $^{36}\text{Ar}_{\text{tr}}$ -carrier to metal phases provides a tool to fractionate the two carrier phases Q and HL. This study will be extended to the primitive CR2 chondrite Renazzo.

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The isotopic composition of sulfates in rivers the Ljubljanica and the Sava in Slovenia

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The $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ in any river represents a mixture of the sulfur derived from the soil, bedrock, and the atmosphere. It can be modified by biotic processes in the river and its watershed. In principle, the $\delta^{34}\text{S}$ measurements can be used to fingerprint the sources of sulfur and the key pathways of sulfur transformation in riverine ecosystem. Combined measurements of the isotopic composition of sulfur and oxygen in sulphate further constrains the possible sources, key processes, and pathways. The Ljubljanica river: 1. Underground waters of the mountain massif are characterized by sulfur with $\delta^{34}\text{S}$ value +5,88 permil and by oxygen with $\delta^{18}\text{O}$ value of +7,36 permil. The concentration of sulfate in spring water (Mocilnik) is about 4,8 mg/l. 2. At the sampling point Podpec the increase of sulfate concentration (12,56 mg/l) was observed and small enrichment of sulfates in light isotopes. 3. On the basis of our results it seems that the tap water is coming from source other than the underground waters of the mountain massif. Their sulfates have isotopically lighter sulfur and oxygen ($\delta^{34}\text{S} = +2,00$ permil and $\delta^{18}\text{O} = +5,27$ permil, respectively). The Sava River: 1. the Sava Bohinjka at sampling point Bohinjska Bela practically does not contain sulfates (0,80 mg/l), while the sulfate concentration of the Sava Dolinka at sampling point Dovje was 8,67 mg/l with $\delta^{34}\text{S} = +10,06$ permil and $\delta^{18}\text{O} = +10,64$ permil. 2. Starting from the sampling point Okroglo the systematic enrichment of sulfates in the light sulfur and oxygen isotopes was observed along the course of river. We suggest that the primary source of sulfates was antropogenic sulfur emitted to the atmosphere and circulated in the natural cycles for an extended period of time.

Iron isotope fractionation by the human body, animals and plants

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Recent advances in measurement of iron isotopes triggered a debate on the utility of this tool for tracing the presence of Fe-metabolising microbes in the environment. However, the work of Beard, Johnson, Bullen, Anbar, Matthews, Brantley, and others rapidly demonstrated that inorganic Fe isotope fractionation can be larger than that from microbial activity. We have studied the iron isotope composition of the human body and dietary Fe sources and found that mammals produce the largest natural Fe isotope fractionation observed to date.

After microwave decomposition and Fe purification, Fe isotopes were measured by a Nu Plasma MC-ICPMS. Results are presented as $\delta^{56}\text{Fe}$ relative to IRM14 (2σ St dev = 0.1‰). Some plant products (wheat, rye, and spinach, $\delta^{56}\text{Fe}=-0.1$ to -0.4%) are only modestly lighter than 40 samples of various soil types ($\delta^{56}\text{Fe}= -0.1$ to $+0.3\%$). Other plants (rice, lentils, green beans, soy beans, peas, $\delta^{56}\text{Fe}= -1$ to -1.5%) are even lighter. Possibly these plants incorporate the mobilised Fe in soils which is sometimes as light as -2.5% . Alternatively, iron is fractionated during uptake from the soil.

Interestingly, muscle tissue from seafood (shrimp, tuna) is relatively unfractionated (-0.2 and -0.6%) but muscle tissue from land animals (beef, chicken, pork) is as light as -2 to -2.6% . Human muscle tissue is as light as -2.1 to -3.3% , while the human liver appears to contain heavier Fe than the rest of the body (-1 to -1.6%). Human blood samples contain very light Fe throughout, where $\delta^{56}\text{Fe}$ is -2 to -3.1% . The lightest natural Fe measured to date is human hair (-3.6%).

We explain the light Fe in mammals by preferential absorption of light Fe isotopes in the intestine. Only ca. 10% of dietary Fe is absorbed by humans, with the complementary heavy Fe excreted in feces. Fe absorption involves a series of steps, including reduction of Fe(III) to Fe(II) or binding of Fe by transport proteins. Both equilibrium and kinetic fractionation effects are possible. A slight difference between female blood (mean $\delta^{56}\text{Fe}=-2.43\%$) and male blood (-2.75%) correlates with higher Fe losses/Fe absorption in females (1.3mg/day versus 1.0mg/day in males). However, mass balances suggest that the difference in $\delta^{56}\text{Fe}$ is not caused by the difference in Fe turnover alone. Rather, each individual appears to absorb Fe with a unique Fe isotope fractionation factor, which tend to be more pronounced for males.

Given the residence time of Fe in humans is ca. 5 years, Fe isotopes represent a long-term fingerprint of biochemical Fe metabolism. The heavy isotopes offer considerable promise for medical applications.

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Plagioclase peridotites : subsolidus breakdown or trapped melt?

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About 20% of all abyssal peridotites contain plagioclase (Dick, 1989), but its origin has long been the subject of controversy. Hamlyn & Bonatti (1980) proposed a subsolidus breakdown of the spinel following the equation $\text{cpx} + \text{opx} + \text{Al-sp} = \text{plag} + \text{ol} + \text{Cr-sp}$. Other authors proposed that plagioclase crystallized from a trapped melt at low pressures (e.g. Dick, 1989).

During the AMORE cruise in summer 2001 very fresh peridotites were sampled in the amagmatic area at $84^\circ 37.5' \text{ N}$ and $004^\circ 13.9' \text{ E}$ (PS 59-235). This dredge haul contains about 30% plag-bearing and 70% plag-free peridotites. Their very low degree of alteration allows the compositions of all phases to be measured and so hopefully to distinguish between the two hypotheses.

This study is based on three samples, one plag-free as reference and two with different amounts of plagioclase. Both contain plag-opx-symplectite reaction textures surrounding cpx, one of these also includes spinel.

In sharp contrast to the homogeneous and relatively fertile plag-free sample, all phases of the plag-bearing samples show strong disequilibrium, producing a large compositional range.

Compositional maps of the plag-bearing samples reveal strong compositional gradients in cpx as strong aluminum depletion on the plag-cpx contact as well as enrichment of Ti and Cr along the rim, maybe because of cpx volume change.

The an-content of the plagioclase ranges from 76 up to 94 with highest contents in the symplectite structure. This suggests that the symplectite is a preexisting in-situ breakdown texture, and the subsequent plagioclase crystallization occurs in a system with a higher Na-activity.

In contrast, the TiO_2 -content in most phases of the plag-bearing samples plots along two different trends with respect to Cr#, which could also be evidence for the presence of exogenous melts.

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Life span of a Cu-(Au-PGE) porphyry deposit using high-precise U-Pb single zircon dating, example: Elatsite, Bulgaria (Bulgaria)

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Single zircon analyses from several porphyry dykes bracketing the time of formation of the Elatsite porphyry Cu-Au-deposit (Bulgaria) were dated by high-precision U-Pb isotope analysis, using thermal ionisation mass spectrometry (TIMS). On the basis of crosscutting relationships, and the mineralogy and geochemistry of igneous and altered rocks, five dyke units are distinguished. The earliest porphyry dyke is associated with, and overprinted by, the main stage of ore-related veining and potassic alteration. U-Pb analyses of zircons yield a mean $^{206}\text{Pb}/^{238}\text{U}$ age of 92.1 ± 0.3 Ma, interpreted to reflect the time of intrusion. Zircons of the latest ore-forming dyke, crosscutting the main stage veins but still associated with minor potassic alteration and veining, give an intrusion age of 91.84 ± 0.3 Ma. Thus, ore mineralization is confined by individually dated igneous events, indicating that the entire time span for the ore-forming magmatism and high temperature hydrothermal activity extended over a maximum duration of 1.1 Ma, but probably much less. Zircon analyses of a late ore dyke cutting all ore veins and hosting pyrite as the only sulfide mineral give a concordant $^{206}\text{Pb}/^{238}\text{U}$ age of 91.42 ± 0.15 Ma. Based on spatial relationships of the magnetite-bornite-chalcopyrite assemblage with coarse-grained hydrothermal biotite and K-feldspar, a Rb-Sr age of 90.55 ± 0.8 Ma is calculated using the two K-rich minerals. This age is interpreted as a closing stage for the Rb-Sr system at $T \approx 300$ °C consistent with published K-Ar data. Therefore the entire lifespan of the magmatic-hydrothermal system is estimated to have lasted about 1.2 Ma. Soon after, the Cretaceous complex was exposed by erosion, as shown by palaeontologically dated (Turonian; 91 – 88.5 Ma) sandstones containing fragments of porphyry dykes.

Geochemical discrimination ratios suggest a mixed mantle and crustal source of the Cretaceous magma. Isotope analyses of Sr, Nd and Hf confirm the conclusion that all porphyry rocks within and around the Elatsite deposit originate from an enriched mantle source at Cretaceous times, with crustal contamination indicated by moderately radiogenic Pb.

Some genetic characteristics of pegmatite veins from the Pohorje Mountains (Slovenia)

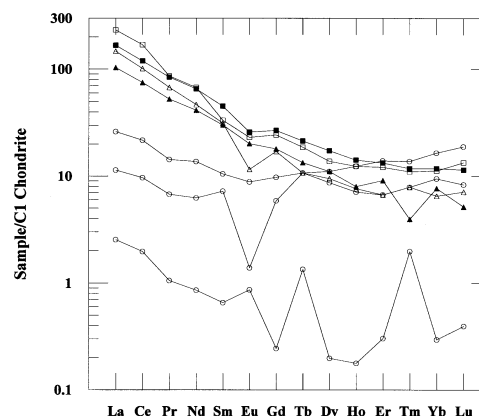
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In the easternmost part of the Periadriatic lineament, east of the Lavantal line in Slovenia, lie Tertiary igneous rocks of the Pohorje Mountains. They are of calc-alkaline affinity and of a compositional range which extends from gabbro to granite. Several up to 2 m thick granite pegmatite veins followed later by emplacement of rare lamprophyre dikes have invaded these rocks.

On the basis of field observations, petrological, geochemical and stable isotope data, we can conclude that the pegmatite veins belong to several generations formed during the final stage of magmatic evolution of this area at a temperature below 570 °C. The mineral composition of the pegmatite veins is very simple. The essential components are potash feldspars, sodic plagioclase and quartz. There are also minor amounts of muscovite, tourmaline, beryl and secondary calcite. The REE chondrite normalized pattern shows a negative Eu anomaly of different size and progressive enrichment with REE from gabbroic to granitic rocks, as well as a considerable and a highly variable depletion of REE abundances in pegmatite veins (Fig.1). The youngest pegmatite veins containing tourmaline and beryl exhibit the lowest REE concentrations and a positive Eu anomaly. This depletion is most probably the result of REE enrichment in the residual melt from which the lamprophyre dikes, with an REE content similar to that of granitoid rocks, crystallized in the final stage after the formation of the pegmatite veins.

Figure 1: Chondrite-normalized REE patterns for the igneous rocks gabbro-cizlakite -▲, granodiorite -△, dacite -□, pegmatite -○, lamprophyre -■ (average samples).



Stable isotope ratios of sedimentary organic matter as indicators of mountain lake trophic state changes

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Stable carbon and nitrogen isotope investigations have proven to be a powerful tool in studies related to C and N cycles in aquatic environments. Organic matter produced and sedimented at the lakes bottom represents a time-averaged integration of processes affecting stable isotopic composition. The use of stable isotopes of bulk sediment organic matter (SOM) to study past environmental conditions is based on the assumptions that SOM originates from primary production in the water column and that the isotopic ratios reflect those of organic matter produced in the water column (Schelske and Hodell, 1991). If these assumptions are valid, then the stable isotopic composition of sediments should be a function of nutrient-driven productivity or trophic state in lake (Gu et al., 1996).

In the present study we explore the applicability of C and N stable isotope signatures in SOM to trace changes in lake trophic state in four mountain lakes in NW Slovenia. Obtained results are summarized in the table below.

Lake	trophic state	$\delta^{13}\text{C}$ [‰]	$\delta^{15}\text{N}$ [‰]
Zgornje Krisko jezero	oligotrophic	-19.8 to -15.2	-1.0 to +0.9
Jezero v Ledvicah	oligotrophic to mesotrophic	-26.3 to -22.4	-3.0 to +1.6
Krnsko jezero	eutrophic	-31.5 to -24.9	-1.2 to +2.4
Jezero na Planini pri Jezeru	eutrophic to hypertrophic	-36.0 to -29.6	+1.3 to +2.9

Higher $\delta^{13}\text{C}$ values are associated with lower $\delta^{15}\text{N}$ values and are characteristic of oligotrophic lakes, while lower $\delta^{13}\text{C}$ values are associated with higher $\delta^{15}\text{N}$ values that are characteristic for eutrophic lakes. The latter can be explained by processes such as bacterial methanogenesis and N_2 fixation by cyanobacteria.

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Silicon isotopic composition of sponge spicules determined by MC-ICPMS

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Introduction

Silicon isotopes are of interest for a large range of topics in the earth sciences, ranging from continental weathering to biological productivity in the oceans. We present new data on silicon isotopes measured by a high-resolution double focussing ThermoFinnigan Neptune MC-ICPMS. In high-resolution mode, this instrument is capable of separating the $^{12}\text{C}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}$, $^{14}\text{N}_2\text{H}$ and $^{14}\text{N}^{16}\text{O}$ interferences from ^{28}Si , ^{29}Si and ^{30}Si . The reproducibility of $^{30}\text{Si}/^{28}\text{Si}$ ratio on a 10 ppm silica standard during 3 hours is better than 0.17‰, whereas the mass bias is in the order of $12 \pm 1\%$. The sensitivity for ^{28}Si is about 1V/ppm in HR mode.

In this study, we report ^{30}Si on sponge spicules as a possible indicator for the fractionation of silicon isotopes between dissolved silicon and biogenic opal. We selected sponges because they have a large geographical distribution, grow slowly and incorporate only a small fraction of the marine dissolved silicon (Douthitt, 1982).

Results and Discussion

We measured the ^{30}Si of five modern shallow-water sponges of the species *Halichondria panicea* from different settings and regions, varying from arctic waters around Spitsbergen to tropical Indonesia. The ^{30}Si range is at least 3.2‰, and does not correlate with the temperature of the sampling region. We also determined the ^{30}Si of a mixed assemblage of deep-water sponge spicules from Holocene deposits off East Greenland. The absolute ^{30}Si values are different from the modern shallow-water sponge values, however the ^{30}Si range is similar, 3.6‰.

The results from *Halichondria panicea* and the deep-water sponges suggest that there are considerable differences in the isotopic composition of dissolved silicon in surface and deep waters. This confirms earlier results on diatoms and dissolved silicon by De La Rocha et al. (2000).

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Oxygen isotope ratios in alkaline basites from Kuznetsky Alatau ridge (South Siberia)

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Introduction

Alkaline basites investigated by us are located in the northern part of the Kuznetsky Alatau ridge (South Siberia). These rocks form a lot of minor multiple intrusions and can be classified in four major groups: middle-alkaline gabbro, theralites and feldspar-bearing foidolites, foidolites (urtites and ijolites), nepheline syenites. According to our data veins of comagmatic calcite carbonatites are established in the one of such intrusions.

Results

We studied an isotopic composition of oxygen in rock-forming clinopyroxenes, plagioclases, nephelines (40 mineral fractions) and whole-rock (22 samples) from some alkaline basic massifs (MI 1201V mass spectrometer, standard deviation $\pm 0,2$ ‰ relative to SMOW, analyst is B.G. Pokrovsky, IGEM RAS, Moscow). Mean ^{18}O values in whole-rock samples consistently increased from 8,4‰ in more ancient gabbro to 9,6‰ in theralites and foidolites and to 10,5‰ in more young nepheline syenites. The similar trend to range mean ^{18}O values is revealed for clinopyroxenes in the sequence from gabbro (7,2‰), to theralites and feldspar-bearing foidolites (8,9‰) and to foidolites (9,3‰) except one data (8,2‰) measured in nepheline syenites. Plagioclases and feldspars have a tendency to increase of oxygen isotopic parameters also (from 8,6‰ in basic rocks to 10,6‰ in nepheline syenite). The rock-forming nepheline is characterized by similar ^{18}O values (10,0-10,7‰). Nevertheless a sharp violation of isotopic equilibrium between minerals isn't observed in spite of enough high level of total contamination in rocks. In this case the crustal material seems to enter in the magmatic system during the liquid stage. The fractionation of oxygen isotopes (^{18}O) between co-existing clinopyroxenes and plagioclases (0,8-2,4) or clinopyroxenes and nephelines (0,5-1,9) is assumed a conservation of oxygen isotope system by wide-range temperature from 870-890°C to 360-410°C.

Conclusion

Results of these researches can show a progressive crust contamination of parental mantle alkaline basic magma during its uplifting and differentiation. For our example, these processes were caused a transformation of not only oxygen but also Rb-Sr-isotopic system in rocks. Most effect of contamination is observed in carbonatites ($I_{\text{Sr}}=0,7057-0,7065$; $^{18}\text{O}=11,8-15,5$ ‰) associated with alkaline rocks. According to our preliminary data parameters of Sm-Nd isotopic system in studied alkaline rocks and carbonatites ($\text{Nd}_T=5,0-7,2$) unlike oxygen and strontium aren't altered and can show a depleted mantle source of parental magma.

