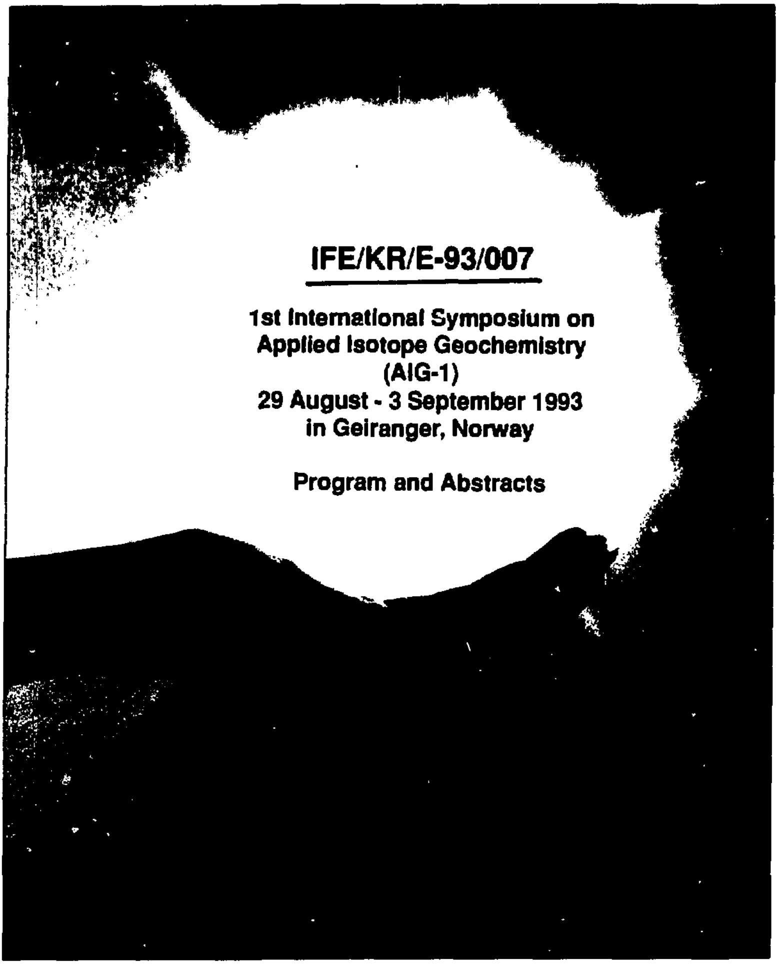

IFE/KR/E-93/007

1st International Symposium on Applied Isotope Geochemistry (AIG-1)

29 August - 3 September 1993
in Geiranger, Norway

Program and Abstracts

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ABSTRACT

The publication is a compilation of abstracts from the "1st International Symposium on Applied Isotope Geochemistry (AIG-1)" in Norway. The symposium was the first of its kind taking up different applications of most of the available isotopic systems and thus covered a wide range of topics from: 1) Water resources, hydrology, geomedicine and environmental problems, 2) Petroleum exploration and production, 3) Mineral exploration and 4) Analytical methods.

KEY WORDS Isotopes; applications; symposium; Geiranger, Norway

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Introduction

Already during, but especially after the 1st International Symposium on Applied Isotope Geochemistry (AIG-1), there has been a great demand for the Abstract Volume handed out to the participants at the meeting. We have therefore decided to reprint the Volume and have also given it an ISBN number for citation.

The Abstract Volume is arranged as follows:

1. It starts with the Symposium Program which is divided into different sections.

2. Within each session the name of the participating author, giving the talk, is written in bold.

3. The Abstract Volume is not paginated, but arranged alphabetically after the participating author (in bold).

4. The Abstract Volume ends with names and addresses of the participants.

3/4

Welcome to

1st International Symposium on Applied Isotope Geochemistry
(AIG-1)

29 August - 3 September 1993

Geiranger, Norway

Dear Participants

During the last decades there has been an increasing interest in the application of isotope systems on a variety of scientific fields. Isotopic methods are now, for example, applied in petroleum exploration problems like stratigraphy and as natural tracers to describe and test migration between reservoirs. These methods are also increasingly used in the study of interaction between the environment and anthropogenic processes, geomedicine and on cultural heritage problems. Many of these achievements would not have been possible without the advances in analytical techniques and instrumentation.

It is thus fair to say that isotope geochemistry plays a successively increasing role in solving problems in many new disciplines. It is therefore of greatest importance to have this forum of researchers treating problems on an interdisciplinary level.

We have received a large number of contributions for the symposium. The quality of the contributions are high and it is exciting to see the many interesting papers which are to be presented both orally or as posters. The scientific committee has had a rewarding task in compiling the papers into an interesting program.

We hope to offer you a successful meeting of high scientific quality with challenging and fruitful discussions where new ideas on how to solve important applied scientific problems by isotope techniques should be generated.

Arne Råheim
Chairman of the Organising Committee

Sponsors

(in alphabetical order)

Elf Petroleum Norge AS

Institutt for energiteknikk

International Association of Geochemistry and Cosmochemistry

International Science Foundation

Royal Ministry of Foreign Affairs

Statoil

Monday 30 August 1993
Water resources, hydrology and environmental problems

0900	*Opening of the Conference*
0930 - 1000	CO_2 content of ancient atmospheres based on kerogen isotopes. **C.Clayton**
1000 - 1030	Stable isotope geochemistry applied to paleoclimatological and greenhouse gas problems. **T.V.Segalstad**
1030 - 1100	*Coffee*
1100 - 1130	Seasonal dynamics of the River Elbe: Fluxes from carbon- and strontium-isotopes. **A.Diener** & J.Veizer
1130 - 1200	Carbon- and strontium-isotopes in the river Danube and its tributaries: Tracers for geogene and biological controls over water chemistry. **F.Pawellek** & J.Veizer
1200 - 1230	Isotopic Evidence for Methane Formation and Decomposition in Marine and Freshwater Environments. **E.Faber,** P.Gerling, A.Hollerbach, W.Stahl & H.W.Schröder.
1230 - 1400	*Lunch*
1400 - 1430	Strontium Isotope Characterization of Ground-Water Flow Systems at Yucca Mountain, Nevada, USA. **Z.E.Peterman** & J.S.Stuckless
1430 - 1500	δD, $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$, and $\delta^{87}Sr$ Systematics in Ground Water and Hydrogenic Deposits at Äspö, Sweden. **B.Wallin** & Z.E.Peterman
1500 - 1530	The $^{87}Sr/^{86}Sr$ ratio as an environmental tracer. **G.Åberg**
1530 - 1600	*Coffee*
1600 - 1630	Source and pathways of lead in humans from the Broken Hill Mining Community. **B.L.Gulson,** K.J.Mizon, A.J.Law, M.J.Korsch, J.J.Davis & D.Howarth
1630 - 1700	Mobility of sulphur during early diagenesis in freshwater peat: Evidence from stable sulphur isotopes. **M.Novak** & R.K.Wieder
1700 - 1730	Sulphate Isotope Signatures in New Zealand Rivers. **B.W.Robinson** & S.H.Bottrell
1730 - 1800	Areas after open cast lignite mining and including waste deposits - an isotope hydrological case study from Kanena/Halle, Germany. **R.Trettin,** W.Richter, G.Strauch, P.Kowski & W.Glässer

Tuesday 31 August 1993
Petroleum exploration and production

0900 - 0930	Late diagenesis and thermal history of the Middle Ordovician St.Peter sandstone, Michigan Basin: Some evidence from illite K/Ar ages and $^{18}O/^{16}O$ ratios. **J-.P. Girard** & D.A.Barnes
0930 - 1000	Early and late diagenetic illites from the Middle Riphean Debengda Formation, Northern Siberia: Rb-Sr evidence. **I.M.Gorokhov**, M.A.Semikhatov, A.V.Baskakov, N.N.Melnikov, T.L.Turchenko, T.A.Ivanovskaya, E.P.Kutyavin & O.V.Yakoleva.
1000 - 1030	Deduction of diagenetic reaction mechanisms and transport patterns from isotope geochemistry. **H.Johansen**, A. Råheim & I.K. Iden.
1030 - 1100	*Coffee*
1100 - 1130	Heterogeneity of waters within one formation as a result of mixtures from two sources; and a new method for determining compositional variation. **M.Coleman**
1130 - 1200	Mixing and dilution of brines, Berea sandstone, Ohio; Chemical and isotopic evidence. **G.Faure**, J.V.Freeman & N.F.Knapp
1200 - 1230	Mapping of reservoir hydrodynamic systems isotope ratios- "an application of the natural $^{87}Sr/^{86}Sr$ isotopic tracer". **A.Råheim**, G. Åberg & H. Johansen.
1230 - 1400	*Lunch*
1400 - 1430	Multiple Origins of Petroleum in the Viking Graben. **H.M.Chung**, G.E.Claypool, C.C.Walters & G.R.Gormly
1430 - 1500	Stable isotopes (H,O,C): Generation and migration of hydrocarbons in evaporates (North Caucasus salt deposits as example). **Y.A.Fedorov**
1500 - 1530	Use of Stable Isotope Data to Monitor *In Situ* Processing of Oil Sands. **H.R.Krouse**, I.Hutcheon, M.Shevalier, C.Nahnybida & H.Abercrombie
1530 - 1600	*Coffee*
1600 - 1630	Using stable isotope data to define the causes of carbonate trapping. **P.Wagner**
1630 - 1700	Isotope Composition of Atmospheric Sulphate Near Sour (H_2S-rich) Gas Processing Facilities in Alberta, Canada. **A-L.Norman** & H.R.Krouse
1700 - 1730	Carbon Isotope Fractionation During Oil To Gas Cracking. **C.Clayton**
1730 - 1800	Carbon isotope composition of methane in crystalline rocks of the Silian impact structure - Sweden. T.Laier & **A.A.Aldahan.**

Wednesday 1 September 1993
Mineral exploration

0900 - 0930	The Grenville-gold Connection and the Dating of Deformation. **T.Krogh**
0930 - 1000	The Grenvillian-Alpine evolution of Pb-Zn mineralization in Spitsbergen: Pb-isotope evidence for the post-Tertiary rejuvenation. **S.I.Turchenko** & L.A.Neymark
1000 - 1030	*Coffee*
1030 - 1100	Stable Isotope Study of Graphite Deposits in the Bohemian Massif. **J. Hladikova** & B.Kribek
1100 - 1130	Application of silicon isotope study in ore genesis. **T. Ding**, S .Jian, D. Wan. Y. Li & J. Li
1130 - 1200	Sulfides, sulfates and searching for ore: An isotopic approach. **A. S. Andrew**
1200 - 1230	Depositional and diagenetic $\delta^{34}S$ signatures in 2.0 Ga-old "black shales": Isotopic constraints for the sulphur source of ultramafic-hosted Ni-Cu sulphide ores, Pechenga, Russia. **V.A.Melezhik** & L.N.Grinenko
1230 - 1400	*Lunch*
1400 -	*Excursion*

Thursday 2 September 1993

Analytical methods. Water resources, hydrology and environmental problems

0900 - 0930	Reproducibility of the isotope-GC technique: Examples and data taken from organic geochemical samples. **M.Østbye-Hansen,** K.A.Bakken, R.P.Moe & M.Bjorøy
0930 - 1000	Stable isotopes: new inlet systems and new opportunities. **C.B.Douthitt**
1000 - 1030	Measurement of intracrystalline fractionation of oxygen isotopes between hydroxyl and non-hydroxyl sites in kaolinite by thermal dehydroxylation. **J.-P. Girard** & S.M.Savin
1030 - 1100	*Coffee*
1100 - 1130	Stable Carbon Isotopes on Methane in Nanoliter Quantities. **E.Faber,** E.Sohns, J.Poggenburg & P.Gerling
1130 - 1200	Nitrogen Isotope Determination on Minute Gas Quantities. **E.Sohns,** P.Gerling, G.Everlien & E.Faber
1200 - 1230	Isotope Abundance Measurements of Microgram Quantities of Sulphur. **A.L.Norman,** M.Wieser, H.R.Krouse & A.Giesemann
1230 - 1400	*Lunch*
1400 - 1430	Increase of resolution in U-Pb dating using refined mineral separation techniques. **S.A.Sergeev** & R.H.Steiger
1430 - 1500	Boron Concentration and Isotope Abundance Measurements. Comparison of Negative Thermal Ionization Mass Spectrometry and Inductively Coupled Plasma Techniques. **M.Wieser,** H.R.Krouse, S.Iyer, H.J.Abercrombie & R.A.Davidson
1500 - 1530	Environmental isotopes in flood flows in a major Australian river. **A.S.Murray,** J.M.Olley, L.Olive, P.J.Wallbrink & G.Caitcheon
1530 - 1600	*Coffee*
1600 - 1630	^{10}Be measurements with the Uppsala tandem accelerator and some geological applications. A.A.**Aldahan** & G.Possnert
1630 - 1700	Isotope studies within the hydrogeochemical site investigations by Teollisuuden Voima Oy, Finland. **M.Snellman** & P.Ruotsalainen
1700 - 1730	Redistribution of radium and thorium isotopes as a result of soil formation. J.M.Olley & **A.S.Murray**
1730 - 1800	Modelling Solute Transport in Catchments Using Unit Hydrograph Techniques. **C.J.Barnes** & M.Bonell
1800 - 1830	Final discussion

Posters

Some analytical potential of the Accelerator Mass Spectrometer at Uppsala University. **A.A.Aldahan** & G.Possnert, Institute of Earth Sciences, Uppsala University, Box 555, S-751 22 Sweden.

Mineralization in magmatic systems: Oxygen isotope evidence. **A.S.Andrew**

Origin of natural gases from the Vienna basin and Carpatian Foredeep, Czech Republic. **F.Buzek** & M.Michalícek

Three component model of runoff generation, Lysina catchment, Czech Republic. **F.Buzek**, J.Hruska & P.Kram

Carbon isotope study in underground gas storage reservoirs. **F.Buzek**

Estimation of actual residence time of water in a deep stratified artificial lake using ^{18}O measurements. **F.Buzek** & M.Rudis

Seasonal dynamics of the River Elbe: Fluxes from carbon- and strontium-isotopes. **A.Diener** & J.Veizer

Anthropogenic transformation of chemical and isotopic composition of the Aral Sea and natural water of its basin. **Y.A.Fedorov** & A.M.Nikanorov

The contribution of tin-lead capsules as a source of lead in wine. **B.L.Gulson** & T.H.Lee

Stable carbon and hydrogen isotope studies of natural gases from the Polish Flysch Carpathians. **M.Kotarba**

Retention of Deposited Sulphate in Acid Forest Soils Determined by Sulphur Isotope and Mass Balances. B.Mayer, **P.Fritz,** H.R.Krouse, J.Prietzel & K.-E.Rehfuess

The C-isotope perturbation at the Permian/Triassic boundary: Evidence of a greenhouse overshoot? R.Morante & **A.S.Andrew**

^{10}Be in a 5.4 Ma sequence of loess-fluvial-lacustrine sediments from North China: *chronologic and climatic implications.* **S.Ning,** A.A.Aldahan, Y.Haiping, G.Possnert & L-.K.Köningsson, Institute of Earth Sciences, Uppsala University, Box 555, S-751 22 Sweden.

Carbon- and strontium-isotopes in the river Danube and its tributaries: Tracers for geogene and biological controls over water chemistry. **F.Pawellek** & J.Veizer

AMS radiocarbon applications in environmental and climatic sciences. **G.Possnert,** Institute of Earth Sciences, Uppsala University, Box 555, S-751 22 Sweden.

Analysis of $^{87}Sr/^{86}Sr$ in silicates using a laser microprobe system with benzene (C_6H_6) vapour as *reducing agent.* D.E. *Stijfhoorn* & A **Råheim.**

Fine fractions of argillites for the Rb-Sr dating: Separation, XRD and TEM studies. **T.L.Turchenko,** I.M.Gorokhov, N.N.Melnikov & G.V.Kotov

Carbon isotopic composition of whewellite ($CaC_2O_4 \cdot H_2O$) from different geological environments and its significance. **K.Zák** & R.Skala

1st International Symposium on Applied Isotope Geochemistry (AIG-1)
Geiranger, Norway, 29 August - 3 September 1993

Laser determination of weathering depth and provenance by carbon and oxygen isotopes.

G.Åberg, D.E.Stijfhoorn, A.Råheim & R.Löfvendahl

Some analytical potential of the Accelerator Mass Spectrometer at Uppsala University

Ala Aldahan [a,b] and Göran Possnert [a]

[a] The Svedberg Laboratory, Uppsala University, S-751 21 Uppsala, Sweden
[b] Institute of Earth Sciences, Uppsala University, S-751 22 Uppsala, Sweden

We summarize in this abstract the present and near future (two coming years) potential of the Uppsala High Voltage Engineering 6MV EN-tandem van de Graaff accelerator for the analysis of cosmogenic isotopes (Fig. 1). Cosmic ray interaction with the earth's atmosphere results in formation of radiogenic isotopes that have half-lives extending from parts of a second to millions of years. Of these some happened to be ideal for covering a part of the geological time scale. Examples are ^{14}C (≈50000 y), ^{36}Cl (≈3 Ma), ^{26}Al (≈7 Ma), ^{10}Be (≈15 Ma), ^{53}Mn (≈35 Ma) and ^{129}I (≈150 Ma). The introduction of AMS technique in analysing these cosmogenic isotopes has opened a wide research front for the geological community. The most crucial advance brought by the AMS is the high sensitivity and as a result a relatively small amount of sample compared to the conventional methods. This led to new applications and more refind details. Our AMS possibilities at Uppsala include analysis of :1) ^{14}C with analysis error of <1 % and a sample amount of at least 1 mg carbon. A variety of more than 5000 samples were analysed covering subjects from geology, archeology, hydrology, oceanography and medicine; and 2) ^{10}Be with analysis error of <3 % for a sample having ^{10}Be/^{9}Be ratio above 10^{-12}. The amount of samples needed for the ^{10}Be analysis depends on the studied archive. Thus 50 mg sample is needed for ^{10}Be concentration of 10^{9} at/g (e.g marine and lake sediments) and not less than 1 litre for a water sample that contains at least 10^{4} at/g. We have analysed more than 300 samples for ^{10}Be during the last two years including sediments, volcanics, ice, water, tree wood rings. Our research program for the coming two years aims at expanding research on ^{14}C and ^{10}Be as well as the routine analysis of ^{36}Cl, ^{26}Al and ^{129}I. A new dedicated beam line has already been installed at the tandem facility for the detection of the three latter isotopes.

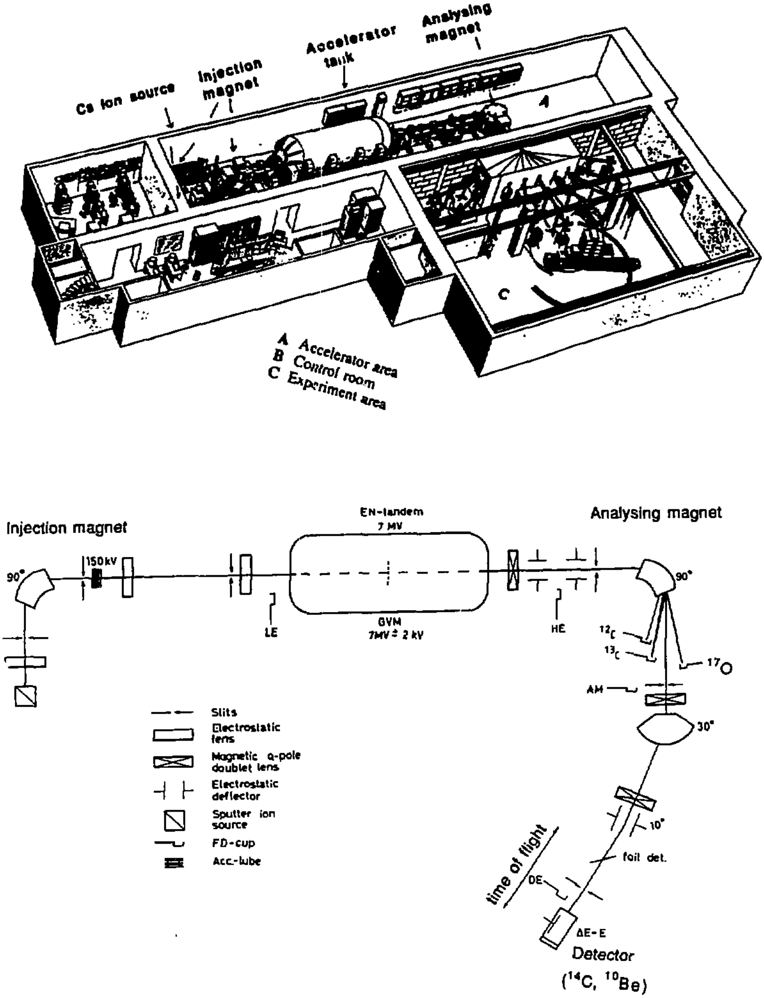

Figure 1 Schematic diagram of the tandem accelerator showing the AMS line.

^{10}Be measurements with the Uppsala tandem accelerator and some geological applications

Ala Aldahan[a,b] and Göran Possnert[a]

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[b] Institute of Earth Sciences, Uppsala University, S-751 22 Uppsala, Sweden

Beryllium-10 is one of the seven Be isotopes of which only ^{9}Be is stable. ^{10}Be has a half-life of 1.5×10^{6} years and decay by electron emission to ^{10}B. About 99% of the ^{10}Be in the earth environments is atmospherically produced by interaction of cosmic rays. The isotope proved, during the last decade, interesting with respect to its mode of occurrence, chemistry and ease of measuring with the accelerator mass spectrometer (AMS). We have now, at Uppsala University, developed routine chemical separation and measurement of ^{10}Be from all geological materials, including water, ice, sediments, rocks etc. An example of the chemical separation of ^{10}Be from solid materials is given in figure 1. The AMS measurement is performed with the Uppsala EN-(nominal 6 MV) tandem Van de Graaff accelerator by adopting the technique of internal beam method. The measurement is based on ^{10}Be/^{17}O proportionality instead of ^{10}B/^{9}Be. Our analysis error is < 3% at ^{10}Be/^{9}Be ratio of 10^{-12}. The applications of ^{10}Be in geological research are vast and we are presently working on some. For example we are studying the distribution of ^{10}Be in a 570 m thick continental sediment profile from North China. The results indicate a potential ^{10}Be-dating back to 5.4 Ma as well as possible climatic-^{10}Be interaction during the change to Quaternary conditions at about 3.6 Ma. To our knowledge, this is the first attempt in applying ^{10}Be chronology on such a long time interval of a continental profile. We have analysed ^{10}Be in two sediment cores (namely Hole 502B of the Ocean Drilling Program and core 290 of the Swedish Deep Sea Expedition) form the North Atlantic in the aim of establishing dating markers and possible environmental-chronological correlation. The results did not fit to a linear decay trend with increasing age for the investigated time interval of 1 Ma (Figs. 2 and 3), but obvious (mostly aperiodic) enhancements in ^{10}Be concentrations appeared. The source of these enhancements is expected to reflect changes in lithology and total oceanic ^{10}Be inventory. Irrespective of cause of enhancements, they could serve as time marker for stratigraphic correlation. A third study of ^{10}Be by our laboratory relates to elucidating magma generation at three eruption in Iceland. Our measurement of ^{10}Be in rhyolitic obsidian from Krafla, Askja and Torfajokull volcanic areas indicates contents above 2×10^{6} at/g.This is significant content for unaltered lava in a rift zone environment like Iceland. A possible source of this ^{10}Be is hydrothermal alteration of subsiding basalt before reaching magma generation zone.

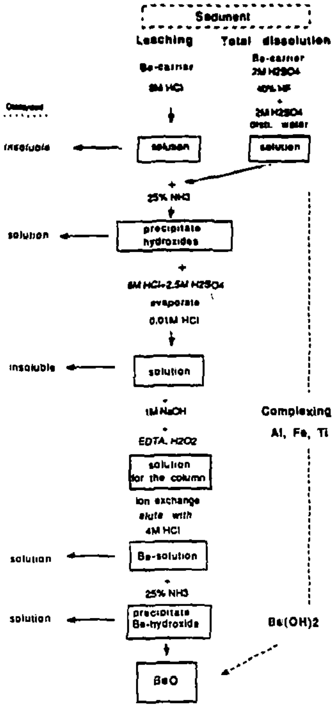

Fig.1-A flowchart for the chemical separation of ^{10}Be *from sediments.*

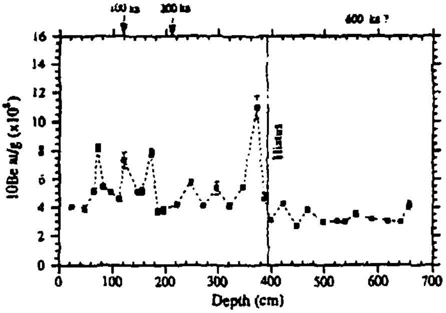

Fig. 2- ^{10}Be versus depth of core 290 showing an expected hiatus. Depth scale below sea bottom at a water depth of 1995 m.

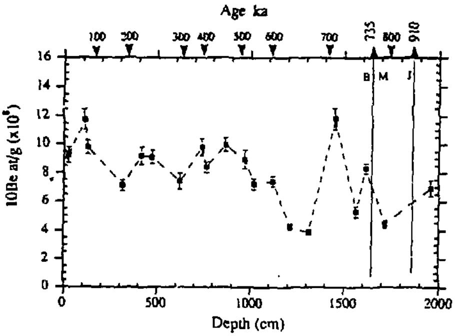

Fig. 3- ^{10}*Be versus depth of Hole 502B. The Brunhes-Matuyama* boundary and the top of Jaramillo are B, M and J, respectively Depth scale is below sea bottom at water depth of 3061 m.

SULFIDES, SULFATES AND SEARCHING FOR ORE: AN ISOTOPIC APPROACH

Anita S. Andrew

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(now at CSIRO Division of Petroleum Resources)

Sulfate minerals are widespread in the Australian surficial environment. Gypsum and alunite occur in both ancient deeply weathered profiles and more modern pedoderms, and are also found in modern lacustrine sediments and adjacent dunes. Sulfate is also a significant anionic species in most Australian groundwaters. The isotopic composition of sulfur in both mineral and aqueous sulfate yields information about the chemical and isotopic composition of Australian groundwaters and may have potential as an exploration indicator for mineralization in weathered and buried terrains.

In the surficial environment, including playas, sulfur isotope variations on a continent-wide scale show that, except where they overlie sulfur-rich bedrocks, there is no correlation between $\delta^{34}S$ values and underlying bedrock types. On a regional scale, in both the Yilgarn Block and central South Australia, the $\delta^{34}S$ values of surficial sulfate vary regularly with distance up to 1000 km from the sea. Airborne sea-salt sulfate ("cyclic sulfate") with a $\delta^{34}S$ value of +21 (permil CDT) is the dominant source of sulfate near coastlines and in places extending hundreds of kilometres inland. The other important source of sulfate ("excess sulfate") is derived from volatile biogenic sulfur compounds (probably with a mean $\delta^{34}S$ value around 0) and is also airborne and largely of marine origin. The entire variation observed is accounted for by a decrease in the "cyclic sulfate" component of airborne-derived sulfate from ≈100% near coastlines to ≈55% in the interior of the continent.

Where bedrock lithologies contain significant sulfur such as sulfide-rich rocks and ores or bedrock sulfate-bearing evaporates, there is often an identifiable bedrock component to the sulfur isotopic signature. The sulfur isotope values of surficial sulfates may be applied to exploration for the search for non-outcropping mineralization that occur as, or are associated with, sulfides and sulfates that have $\delta^{34}S$ values that are distinct from the $\delta^{34}S$ values of regional sulfates (typically +15 to +20). Because the regional surficial $\delta^{34}S$ pattern is established by both sulfate minerals and the dissolved sulfate in groundwaters, our technique may be applied to prospect evaluation, by sampling either regolith or groundwater samples.

Evaluation of surficial sulfate minerals and groundwaters in the vicinity of several non-outcropping base metal and gold deposits suggests:

- Sulfur isotopic values reflect proximity of mineralization. Only in areas with low sulfate groundwaters do we measure the "ore" signature. In areas characterized by saline groundwaters a mixed value is measured.
- Sulfur isotope halo may be orders of magnitude greater than rock geochemical indicators and may be dispersed along paleodrainage channels or along the inferred direction of groundwater flow.

Current industry collaborative studies are investigating:

- The size of isotope haloes and how they compare with other geochemical indicators.
- The preservation of isotopic signatures in groundwater systems.
- Advantages of profile sampling down diamond drill holes compared with sampling to the water table.
- Combined isotopic (S, Pb, Sr, O, H) and element abundance data for recognition of underlying lithologies, especially in areas of transported cover.

In addition to being a new low cost way of exploring for mineral deposits under cover, the results of this research have direct application to environmental studies related to both mining and industrial processes.

MINERALIZATION IN MAGMATIC SYSTEMS: OXYGEN ISOTOPE EVIDENCE

Anita S. Andrew

CSIRO Division of Exploration Geoscience, North Ryde 2113, AUSTRALIA

(now at CSIRO Division Petroleum Resources)

The oxygen isotope fractionation between coexisting minerals in two mineralised *intrusions has been modelled to determine the oxygen isotope composition of the ore* fluids in order to identify their source and to place the mineralizing event within the crystallization history of the magma. The first intrusive complex at Fifield, NSW, was formed from water-poor magma with oxygen isotope fractionations indicative of isotope exchange between minerals only. The second example from the Bushveld Complex in the Republic of South Africa, formed from a water-rich magma and oxygen isotope fractionations indicate exchange with a cooling magmatic hydrothermal fluid.

Platinum-group-element mineralisation is hosted by pyroxenites and peridotites within zoned Alaskan-type intrusive complexes at **Fifield**. The Owendale Intrusive Complex and adjacent Tout Intrusive Complex comprise peridotite, dunite, clinopyroxenite, hornblendite, monzogabbro, monzodiorite and monzonite. Magmatic layering is variably developed in most rock types except dunite and peridotite. Pd-poor and S-poor mineralisation occurs predominantly in cross-cutting clinopyroxene-rich veins and pipes, called P-units within olivine-bearing pyroxenite, biotite pyroxenite, pyroxenite and hornblendite. The veins are commonly monomineralic with textural zoning determined by crystal size and the enrichment of biotite and magnetite in adjacent host rocks.

Oxygen isotope fractionation between clinopyroxene, plagioclase and magnetite pairs indicates high temperature crystallization. $\delta^{18}O$ values of *clinopyroxene and magnetite* from least altered pyroxenites and P-units are 5.5 and 4.1 permil (V-SMOW), respectively, suggesting magmatic crystallisation temperatures as high as 1300°C from a mantle-derived magma with $\delta^{18}O$ of 5.7. All other values plot within the triangular fields defined by these primary values on δ-δ plots, demonstrating closed-system subsolidus exchange to <670°C in a water-poor environment. In pyroxenites and P-units, exchange of ^{18}O has enriched clinopyroxene and biotite and depleted magnetite. In the more felsic rocks, felspar has been enriched and clinopyroxene and magnetite have become depleted in ^{18}O. PGE mineralisation hosted within P-units is apparently magmatic in origin.

Tin-tungsten-rare earth element mineralisation at **Zaaiplaats**, is hosted by the Bobbejaankop and Lease Granites - miarolitic, brick-red alkali felspar granites which form at high levels within the Lebowa Suite of the Bushveld Complex. Pervasive hydrothermal alteration of the granites resulted in replacement of original biotite with chlorite, sericite, carbonate and Ti oxides, development of coarse vein and patch perthite and antiperthite in alkali felspar, and precipitation of hydrothermal minerals in miarolitic cavities. Cassiterite occurs as a cavity filling and replacement mineral in tabular, sub horizontal zones and in shallowly-plunging and branching pipe systems in the granites. Disseminated cassiterite mineralisation exhibits no relationship to fracture systems, and hydrothermal fluids appear to have evolved essentially in situ during crystallisation to produce miarolitic cavities.

Oxygen isotope fractionations between coexisting quartz and alkali felspar are reversed, indicating disequilibrium. On a δ-δ plot quartz-felspar pairs are consistent with felspar and quartz exchanging with an evolving magmatic hydrothermal fluid; the rate of exchange of felspar being much greater than for quartz. Using fluid inclusion temperature estimates and oxygen isotope values from ore and gangue minerals in cavities, pipes and late veins, the calculated $\delta^{18}O$ value of the magmatic hydrothermal fluid decreases from 6 at >500°C to 1.4 permil at 200°C. This data can be used to refine model exchange trajectories on the δ-δ plot that are broadly consistent with the measured oxygen isotope values of sericite, chlorite and cassiterite.

Relatively water-poor magmatic systems like Fifield, oxygen isotope exchange is only between mineral pairs and thereby are characterized by covariation. In more water-rich systems, such as at Zaaiplaats, the relative rates of exchange between minerals become important with disequilibrium and even reversals possible. A system where a magmatic fluid composition buffers the minerals during cooling requires high water/rock ratios and given the water content typical of melts, is highly unlikely in nature. Where the water/rock ratios are still low- moderate, as at Zaaiplaats, the $\delta^{18}O$ value of the magmatic fluid may be lowered by exchange. At both Fifield and Zaaiplaats, the PGE and tin mineralization, respectively are constrained to the earliest phases of crystallization of the magmatic fluid.

Modelling Solute Transport In Catchments Using Unit Hydrograph Techniques

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Abstract

Under certain assumptions of linearity etc., the catchment response function known as the Instantaneous Unit Hydrograph (IUH) can be identified with the apparent distribution of residence times for water within the catchment. Except for very dry conditions, the IUH formalism gives an excellent representation of the rainfall-runoff relationship for many catchments of varied characteristics (size, climatic regime, time scales). For simple solutes, such as the minor (heavy) isotopic species of water, a similar formalism can be developed to predict the output concentrations in runoff, given the input concentrations in rainfall, also employing the residence time distribution.

For this region, variations in rainfall stable isotope concentrations during storms generally greatly exceed variations in streamflow composition, so that explicit temporal modelling of the transfer processes within the catchment is essential. We find a strong inverse correlation between isotope concentrations and rainfall intensity, which confounds any attempt to use simple end-member mixing models.

Using data from a small tropical catchment in Australia (Wyvuri Holding, Babinda, near Cairns) it is shown that the IUH is inadequate as a transfer function for solutes (stable isotopes), and that it is necessary to modify the IUH concept in order to correctly represent the experimental data from this catchment. We show that solutes appear to "see" a much greater storage volume than is suggested by the IUH, and that actual residence times may be two orders of magnitude greater than inferred from the IUH alone. This phenomenon may be responsible for the often-noted discepancy between tracer data showing large proportions of older water in hydrographs peaks, and hydrograph analysis indicating very rapid reponse times, assumed to be due to influxes of current precipitation.

Three characterstic time constants (circa 2 hours, 2 days and several months, respectively) are identified for the catchment from rainfall-runoff time series (15 minute base). The longer response times are identified with the seasonal increase and decrease of the groundwater store, and pertubations of this store caused by individual events; while the shortest is identified with saturation overland flow and through-flow over part of the catchment, caused by a shallow (<50 cm depth) layer of low conductivity.

Analysis of the response from a number of nests of wells, tensiometers and piezometers, give qualitative support to the above conclusions derived

from the catchment hydrographs, but indicate the dominant role which heterogeneity plays in determining the detailed catchment response. We conclude that in this catchment it is not feasible to build the catchment response as an integration of the known hillslope processes (as in current, physically based, models). This is due to difficulty in characterising the catchment heterogeneity, so that it is not possible to determine *a priori* the relative contributions of the different processes (characterised by different time constants). This emphasises the need for high quality catchment data to be obtained **at the same scale as the proposed model.**

ESTIMATION OF ACTUAL RESIDENCE TIME OF VATER IN A DEEP STRATIFIED ARTIFICAL LAKE USING ^{18}O MEASUREMENTS

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The deep, stratified valey reservoir Orlík (South Bohemia, closing 12 107 km^2 of drainage area with only one significant reservoir in) was investigated for estimation of actual residence time of inflow water using ^{18}O measurements. Although the theoretical residence time computed as a ratio of the reservoir volume and the mean water discharge was about 100 days, its real value was estimated from attenuation of the $\delta^{18}O$ values as only 27 days. Simple models as piston flow or completely mixed reservoir were not able to describe the actual flow conditions. Frequent disturbancies of $\delta^{18}O$ which cannot be simply explained were observed at both the in - and out flow values. Then the measured values of $\delta^{18}O$ were smoothed and actual time shifts of input and output have been investigated in relation to the time and discharge through the reservoir. Measured time shifts which corresponds to actual residence times of inflowing water depend on outflow rate and period of the year. At isothermal conditions, about 90 % of the lake volume is available for the flow rate while,with gradual development of stratification, this volume decreases to about 30 % .

ORIGIN OF NATURAL GASES FROM THE VIENNA BASIN AND CARPATHIAN FOREDEEP

F.Buzek and M.Michalíček, Czech Geological Survey,
Malostranské nám.19, 118 21 Prague 1, Czech Republic

Gases accumulated in sediments of the Vienna Basin (VB) and S-E slopes of the Bohemian Massif (Carpathian Foredeep -CF), Czech Republic, have been analyzed for their chemical and carbon isotope composition. Gases have highly variable composition with C_{2+} concentrations ranging between 0 and 20%, nitrogen between 0 and 85%, $\delta^{13}C_1$ between -75 and -30 $^{o}/_{oo}$. Samples were divided into regional groups with respects to their formations. In the Moravian part of VB only microbial gases are autochtonous in Neogene sediments, thermogenic and associated gases migrate from their source rocks (Jurassic marlites). In the Slovak part of VB all gases are autochtonous in Neogene and Mesozoic sediments. In southern part of CF only microbial gases are present with the exception of autochtonous thermogenic gas in the Paleozoic basement. Gases of the middle and northern part of CF migrate from their source rocks (autochtonous Paleogene). Coal gases in northern CF originated in Carboniferous.

THREE COMPONENT MODEL OF RUNOFF GENERATION, LYSINA CATCHMENT, CZECH REPUBLIC

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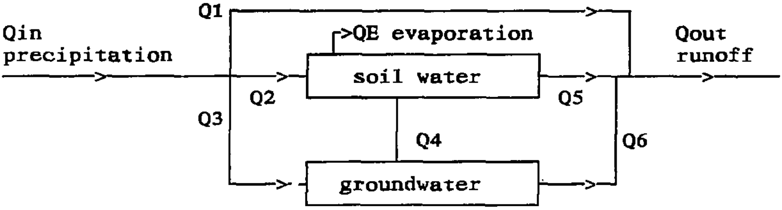
The Lysina catchment represents a forested area very susceptible to acid deposition. It is underlain by a slow - weathering leucocratic granite, soils are podzolized brown earths and peaty glays with small pools of exchangeable basic cations. The most striking feature of streamwater chemistry draining the Lysina catchment is an extremely high concentration of total aluminium (volume weighted mean 66µmol.l) and high concentration of H^+ (pH = 3.87). Strong correlation between stream acidity and streamflow is typical for streamwater. An exponential increase in streamwater acidity with flow during high flow periods could not be explained by a simple two-component model usually used for hydrograph separation.

Our model based on chemical and O-18 analysis of precipitation, soil water and runoff, incorporates a soil water component in streamwater generation. Dissociated organic acids, which are not measured in conventional analyses, help to balance the anion deficit. Organic acids originate from the flux through organic rich soils of the shalowest horizon. The apparent anion deficit increases exponentially with flow rate.

Direct runoff component forms only 5% (in winter) and 8% (in summer) of runoff as calculated from a simple two-component model, to reach maximal 20% in flood episode.As indicated by the low variability in streamwater O-18, indirect component forms most of the runoff. This indirect water component contains variable proportions of soil water and groundwater.

Soil water content (calculated from the apparent anion deficit of streamwater) varies from 0 (at base flow) up to 80% (during flood). In average 40% of streamwater is soil water (32% in winter, 54% in summer). The anion deficit related to soil water was estimated from flood chemistry and verified by an overall ion balance of discharge water.



Model water balance for the Lysina catchment (1991-92)

Period	XI/91-IV/92	V/92-X/92	XI/91-X/92
Volume (mm)			
Precipitation Qin	460	640	1100
Evaporation QE= =Qin-Qout-Qre	217	402	619
Runoff Qout	311	109	420
" direct Q1	13	8	21
" indirect Qout- Q1	298	101	399
soil w. flux Q4+Q5	105	229	334
groundwater flux Q3+Q6	223	60	283
soil infiltr. Q4	7	170	177
soil water c. Q5	98	59	157
direct infiltr. Q3	223	60	283
groundwater c. Q6	200	42	242
g.recharge Qre= =Q3+Q4-Q5-Q6	-68	129	61

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CARBON ISOTOPE STUDY IN UNDERGROUND GAS STORAGE RESERVOIRS

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Chemical and isotopic composition of gases stored in underground gas reservoirs have been used for identification of injected gas migration and reaction. Natural gas injected into depleted gas fields migrated horizontally and vertically into adjacent strata, could be identified in the presence of one or two native gases in the storage.

Town gas (a mixture of about 45% H_2, 25% CH_4, 10-12% CO,CO_2 and N_2) injected into underground acquifer storage was withdrawn with composition (25% H_2, 45% CH_4, 5-7% CO,CO_2 and 10-15% N_2) and considerable loss of stored volume. Extensive use of carbon isotope analysis (of CH_4,CO and CO_2) enabled description of all processes in the storage. Hydrogen losses from methane production could be distingushed from actual losses by leakage.

MULTIPLE ORIGINS OF PETROLEUM IN THE VIKING GRABEN

ABSTRACT

The Kimmeridge Clay Formation is generally recognized as the main petroleum source rock in the Viking graben of the North Sea. The observed variations in crude oil composition are usually viewed as a consequence of the oils having been derived from the Kimmeridge Clay at different levels of thermal maturity. However, our investigation of 117 oils from this area indicates that there are important contributions of petroleum derived from the Upper and Middle Jurassic source rocks, namely the Heather and Brent Formations. In shallow graben centers (e.g., the Beryl kitchen), crude oil is generated mainly from the Kimmeridge Clay, whereas in deep graben centers (e.g., the Troll kitchen), gas and light hydrocarbons are generated from the Heather Formation and Brent coal. Carbon isotopic ratios of gas and gasoline-range hydrocarbons, along with other chemical properties of crude oils, are indicative of their derivation from multiple source rocks. Biomarker properties are used mainly to constrain the levels of thermal maturity of oils. Hydrocarbons generated in the axial parts of the graben system migrate into structurally high Jurassic and Triassic reservoirs near the edges of graben centers mainly through the Middle Jurassic sandstones. Migration pathways for gas and light hydrocarbons are important elements for understanding petroleum occurrence and compositional variations in the Viking graben.

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CO_2 content of ancient atmospheres based on kerogen isotopes

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One of the main controls on $\delta^{13}C$ of kerogen is the availability of carbon dioxide to the primary producing organisms. For aquatic plants this is the dissolved CO_2 in the water, for land plants it is atmospheric CO_2. The $\delta^{13}C$ of ancient kerogen therefore carries with it a record of atmospheric and dissolved oceanic CO_2 concentrations through time.

A collation of carbon isotope data for kerogens analysed during routine geochemical analysis over the past fifteen years reveals many surprises. Secular trends are present in $\delta^{13}C$ of both marine and terrestrial carbon that correlate for the Mississippian-late Jurassic period, and subsequently diverge. This divergence of marine and terrestrial signals during the Cretaceous and Tertiary reflects the spread of angiosperms in the continental environment. When interpreted in terms of paleo-pCO_2, the secular $\delta^{13}C$ trends suggest that ancient atmospheres were significantly enriched in CO_2 relative to the present day (more than 4x for some periods). Highest CO_2 levels occurred during the early Palaeozoic and decreased progressively through Phanerozoic time, although the smooth trend is interrupted during the Carboniferous-Permian period and accelerated during the late Tertiary. The Carboniferous-Permian excursion reflects the spread of photosynthesis on land, while the late Tertiary event appears to be related to changes in global deep water circulation.

The pCO_2 age curves produced from these data closely follow those proposed by Berner based on modelling mid ocean ridge spreading and continental weathering rates. Atmospheric pCO_2 also correlates closely to the accumulation rate of coals through time and the proportion of oceanic sediments represented by carbonates. The general trend towards lower atmospheric pCO_2 apparently compensates for an increase in solar luminosity during this time.

CARBON ISOTOPE FRACTIONATION DURING OIL TO GAS CRACKING

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Isotope fractionation during oil to gas cracking can be modelled as a combination of Rayleigh fractionation and mixing of gas derived directly from kerogen. Variables that have to be constrained are the initial oil to gas ratio, their respective isotopic ratios, the kinetic isotope fractionation factor for each gas component, and the proportion of oil that passes into pyrobitumen rather than gas. Using this model, kinetic isotope fractionation factors have been determined for the formation of methane, ethane, propane and butane. However, when source systems of high and low petroleum expulsion efficiency are compared, there are significant differences in the isotope ratios of ethane at any given extent of oil cracking. These appear to be reflect differences in the rates of gas-to gas cracking in the reservoir as opposed to in the source rock. A laboratory pyrolysis study confirmed that ethane and higher hydrocarbons are anomalously stable in the absence of both kerogen and mineral matrix, suggesting that hydrogen availability is a key rate-determining step in the cracking process. There are also differences in the relative rates of oil aromatisation verses condensation to pyrobitumen between laboratory pyrolysis and natural cracking. When compared, natural, laboratory, and calculated isotopic fractionation factors suggest that natural oil to gas cracking is not a simple free radical reaction as is usually assumed.

Heterogeneity of waters within one formation as a result of mixtures from two sources; and a new method for determining compositional variation

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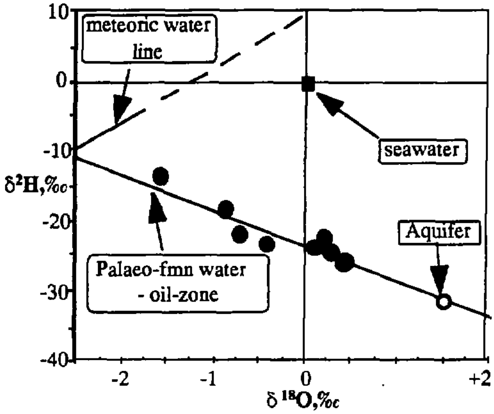
Waters from Forties Field (U.K.C.S.) show a range of compositions which can be interpreted as mixtures of a typical North Sea saline formation water and a much more dilute brine from a mudrock source.

They were co-produced with oil during normal production and, thus, are not contaminated by drilling mud filtrate. Samples were taken covering most of the geographical range of the field over a period of more than five years. Analyses of δ^2H, δ^{18}O, δ^{37}Cl, Na, K, Mg, Ca, Sr, Ba, Cl, Br and SO_4 were made. There is a linear correlation of most chemical and stable isotopic measurements, which is the same for between-well and within-well variations. These data imply that all produced waters are the result of mixing on a field-wide scale of two NaCl brines, the end member compositions are less than 26,000 ppm Cl and about 60,000 ppm Cl. δ^2H, δ^{18}O give a line of negative slope, unlike most other formation water plots, thereby confirming that the waters are mixtures rather than products of evolution by water-rock interaction. The stable isotope values prove that there is no sea-water contamination in the samples. δ^{37}Cl values show that the more saline brine resulted from dissolution of evaporite salts and that the more dilute one contains salts affected by a physical process (diffusion or ion filtration). The most likely origin for such a water is a shale. The precise origin of this water is further defined by the spatial distribution of compositions.

As production continues from any one well, water is drawn up from the underlying aquifer (60,000 ppm Cl) giving successive samples with a higher proportion of water to oil and increasing salinity. When water content becomes unacceptably high, the well is modified to produce from a higher horizon. The consequent reduction in water content is accompanied by a reduction in salinity. This implies that the less saline brine is the residual water of the oil zone and can be interpreted as being the fossil formation water trapped at the time of oil emplacement. Detailed analysis of the production data by Marcus Pallant (Imperial College, London, unpublished data) showed



that there is vertical zonation of composition of oil zone waters with decreasing salinity towards the top of the reservoir. This pattern extends over the whole oilfield.

The most likely candidate for the origin of the less saline brine is the source rock for the oil, since the over-lying seal to the reservoir would not have given the observed spatial distribution of compositions. The hypothesis which best explains all these observations is that less saline brine "migrated" from the shale before oil but followed the same plumbing. It was trapped in the reservoir as a less-saline, warmer and thus lower-density fluid than the pre-existing saline formation water. The reservoir contained the two waters before oil emplacement, probably stratified. Emplacement of oil and its gravity-driven segregation mixed the two waters and fossilized their distributional pattern.

Observation of a fossilized water was possible here because of the extensive production data-base (and possibly because the clean sand and relatively low water content allowed production of the water). The phenomenon of a different water composition trapped in the oil zone might be expected in many cases where the aquifer has changed subsequently but a method for readily measuring water composition in oil zone is needed. In order to apply the method more generally a technique is being developed to sample waters at different depths in the reservoir, at negligible cost. The approach is based on the availability of oil samples from specific depths and that they carry trace quantities of associated formation water. Preliminary results from work by James Thurlow (U. of Reading, unpublished) shows that shaking an oil sample with distilled water extracts the trace water quantitatively. Estimation of the water content of the oil gives an accurate compositional estimate. At present water content is measured by Karl-Fischer method. However, use of a chemical or isotopic tracer in the extractant water will allow a simpler, single step method. Currently we are evaluating the relative merits of Cs, ^{2}H and ^{3}H as tracers to estimate water contents of oils.

SEASONAL DYNAMICS OF THE RIVER ELBE: FLUXES FROM CARBON- AND STRONTIUM-ISOTOPES

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The Elbe river, and its tributaries prior to their confluence with the Elbe, have been sampled in the winter, spring and summer of 1991-1992 at distances of 25 km, with 55 stations along the entire river course. Particular attention was paid to anions that participate in agradation/degradation of organic compounds (e.g. NH_4, NO_3, o-PO_4) and to carbon isotope signal resulting from these processes. In addition, the spring samples were analyzed for Sr-isotopes as a proxy for a geogene signal.

The degradation of organic matter in the Elbe is retarded by direct discharge of poorly treated or untreated communal/agricultural effluents into the river. Ammonium, an intermediate product of N-cycle, is of particular interest because its concentrations may serve as an indicator of the intensity of microbial activity. A plot of temperature dependent O_2-deficit vs. NH_4 concentrations shows clearly seasonally distinct populations. The winter ammonia concentrations are about 5-6 times greater than those of the spring and summer, suggesting that the winter degradation of organic matter is incomplete. This can be partly a consequence of low temperatures. On the other hand, the high winter deficit on O_2 suggests also that the main culprint may be the deficiency in oxygen. Surprisingly, the availability of O_2 in the spring and summer is higher, despite warmer waters and this appears to enhance the rate of bacterial degradation of organics. The postulated additional oxygen source are probably algal blooms. In all likelihood, the increased light intensity, combined with the relatively high concentrations of P and N compounds, enhance euthrophication processes in the river. This seasonal dynamics is reflected also in the carbon isotopic composition of dissolved inorganic carbon (DIC). In winter, the $\delta^{13}C$ varies from -8 to +5‰, suggesting that in the up-river section dissolution of carbonates ($\delta^{13}C = 0 \pm 2‰$) serves as a significant source of DIC. The heaviest values are a reflection of extensively exposed and mined Zechstein sediments and salt deposits within the Elbe catchment area, these having $\delta^{13}C$ as heavy as +8‰. Down-river, however, the isotopically light values are ubiquitous also in winter. In the spring, the microbial degradation of organic matter , caused by warming, lowers the $\delta^{13}C$ of DIC into the -8 to -1‰ range. Surprisingly, the $\delta^{13}C$ in summer rises again to -3 to +6‰, possibly reflecting an enhanced consumption of isotopically light CO_2 by algae, thus, leaving the residual DIC depleted in ^{12}C. Pending completion of the continuing monitoring, the above scenario must be considered a tentative explanation, .

In terms of Sr isotopes, the Elbe can be subdivided into four sections. The headwater geology is dominated by radiogenic crystalline and metamorphic rocks of the Hercynian basement. In the inner-Bohemian area, dominated by Cretaceous sediments, the $^{87}Sr/^{86}Sr$ suddenly decreases to a minimum of ~0.70910, to be stabilized at ~0.71110 after the confluence with the Vltava and Ohre. Such naturally averaged $^{87}Sr/^{86}Sr$ signature is swamped by anthropogenic signal from salt mining discharge into the Elbe by Saale. This anthropogenic signal dominates the river budget until its discharge into the North Sea at Hamburg.

APPLICATION OF SILICON ISOTOPE STUDY IN ORE GENESIS

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A comprehensive study on application of silicon isotopes in research of ore genesis has been undertaken by our group during last 5 years. It is found that *silicon isotope composition can be* used at least in three aspects of ore genetic study.

1. **Distinguish clay minerals of deferent genesis :**

more that 20 samples of clay minerals from China, Italy and United States have been analysed for their silicon isotope composition in our study. It is found that the δ^{30}Si values of weathering kaolinite range form -1.0 to -1.9. In contrast, the δ^{30}Si values of hydrothermal kaolinite range from 0.1 to -0.1, similar to that of granite. The δ^{30}Si values of sedimentary kaolinite are from -0.1 to -1.2, just in between of weathering kaolinite and hydrothermal kaolinite. In view of above characteristics, we may use silicon isotope composition as an indicator to distinguish different origin and environment of clay minerals.

2. **Determine the genetic type of stratiform and stratibound deposits:**

It is well known that there are usually chemical sedimentary rocks, like barite beds or siliceous rocks, occuring in submarine exhalative ore deposits, especially on the margin or the top of their ore bodies. There fore chemical sedimentary siliceous rock is one of important indicators for submarine exhalative deposits. However, there are many kinds of siliceous rocks in nature: quartz sandstone, diatom earth, radiolarian rocks and silicification rocks beside chemical sedimentary siliceous rocks. In the processes of metamorphism, all these rocks can be metamorphosed and become quartzite. In that case their original rock type can not be recognized easily by normal geological methods.

The silicon isotope study is proven very useful in solving this problem. As shown in the Fig. 1 various types of siliceous rocks have their own characteristics of silicon isotope composition. And these characteristics will not change during metamorphism.

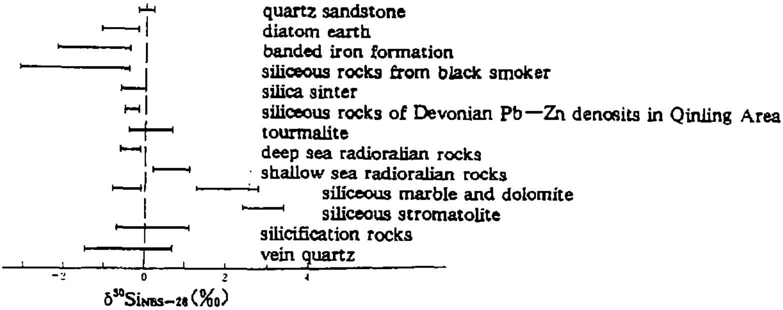

Fig. 1 The δ^{30} Si values of various siliceous rocks

It is obvious from Fig. 1 that the siliceous rocks having negative δ^{30}Si values are most likely the rocks related to submarine exhalative deposits. For example, the chert beds in Archean banded iron formation normally have large negative δ^{30}Si values: -0.9 to -2.2 for BIF in the Gongchangling iron deposit, Liaoning, China; -0.8 to -1.4 for BIF in the Qianan iron deposit, Hebei, China; and -1.6 for BIF in Superior, Canada. The *siliceous rocks from Proterozoic* Baiyun Obo Fe and REE deposit has δ^{30}Si values of -0.3 to -0.8. And the siliceous rocks in the Devonian Pb—Zn deposits in the Qinling area have δ^{30}Si value from -0.3 to -0.6. The modern siliceous sediments from the black smoker of the Mariana Trench have δ^{30}Si values of -0.4 to -3.1.

So the siliceous rocks having negative δ^{30}Si values are thought to be good *inidicators for finding* the submarine exhalative ore deposits, although some diatom earth and deep sea radiolarian rocks have also negative δ^{30}Si values.

3. Tracing the silicon source of quartz vein hydrothermal deposits:

There are tremendous number of hydrothermal deposits occuring as quartz vein type. It is very important to determine the source of material of the quartz vein for the genetic study of this kind of deposits. However, this is not a easy task. Now the silicon isotope study provides us a direct way to determine the source of silicon of this vein quartz.

We have done a lot of work to test this possibility, and find this method is very useful in many cases. For example, the Xihaushan tungsten deposit is a world famous quartz—wolframite vein type of deposit. The wolframite bearing quartz veins occur in the upper part of a granitic stock of Yanshanian age, which intruded into the Cambrian low grade metamorphic argillaceous rocks. Our results show that the Cambrian country rocks have δ^{30}Si values of -0.4 to -0.2, the biotite granite rocks have δ^{30}Si values of -0.2 and -0.1, and the vein quartz has δ^{30}Si values of -0.1 to 0. It seems that these three kinds of geological bodies have close relationship each other on their materials.

Another examples is the Dachang tin and polymetal deposit in Guangxi province. This deposit consists of strantibound ore bodies and vein type of ore bodies occuring in the Devonian limestone and shales. There are granitic stock and diorite dikes in the mining area. For a long period, the tin and polymetal mineralizations are thought to be solely related to the granite, and precipitated from magmatic hydrothermal solution. However, recent oxygen and hydrogen studies show that the ore—forming fluids for tin and polymetal vein mineralization are dominated by the underground meteoric water, which has experinced oxygen isotope exchange with country rocks. In this study the silicon isotope study has been undertaken to check this idea. It is found that the δ^{30}Si values of granite rocks are from -0.3 to -0.1, the δ^{30}Si value of diorite dike is -0.1, and the δ^{30}Si values of chert beds are from 0.8 to -0.2. The δ^{30}Si values of vein quartz vary form -0.1 to 0.5 depending on the silicon isotope composition of country rocks. This condition tells us that the silicon in sedimentary country rocks may be the major source of the silicon in vein quartz.

Stable isotopes: new inlet systems and new opportunities

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A desire to measure $^{13}C/^{12}C$ and $^{15}N/^{14}N$ of individual gas chromatograph (GC) peaks was the motivation that led Hayes and colleagues to develop the technique of *"isotope ratio monitoring"* (*irm*). The growing body of literature reporting on *"compound specific isotopic analysis"* (the measurement of isotope ratios of individual organic compounds) demonstrates how rapidly this new technique has been adopted. Specific accomplishments that can be pointed to include the measurement of $\delta^{13}C$ on individual compounds in whole oils, $\delta^{13}C$ and $\delta^{15}N$ on individual amino acids, and $\delta^{13}C$ of CH_4 in air. *Irm* inlet systems allows accurate and precise isotopic analysis to be carried out on samples some 4 to 6 orders of magnitude smaller than is possible with the dual inlet system; sample sizes are measured in picomoles rather than micromoles.

Now that the hardware required to reach the original goal has matured into a robust commercially available product, researchers concerned with method development have focussed their attention on extending the technique to include a diverse group of sampling procedures, including head space sampling, laser volatilization, and liquid chromatography. The applications that are being actively pursued are isotopic measurements that were previously difficult or even intractable, such as δC of individual plant cells (e.g. spores and pollen grains) and photosynthetic pigments; δC, δN, δO of trace components of air; and *in situ* measurement of δO and δSi in minerals. These new applications are driving the development of a host of new application-specific *irm* inlet systems, which can combine lasers (for non-invasive heating of small volumes), gas or liquid chromatographs (for chemical resolution of individual components of mixtures), head space sampling, chemical traps (for preconcentration of low abundance components of mixtures), and on-line chemical reactions (such as Dumas combustion). There is increased interest in measuring ratios using unconventional gas species including O_2, N_2O, CO and SF_6.

Several well-established analytical techniques are well suited for *irm* inlet systems, including water/CO_2 equilibration and analysis of CO_2 in breath. *Irm* inlet systems are included on ≥50% of all new instruments; approximately 20% of new systems do not even include a dual viscous flow inlet system. These proportions are expected to increase as researchers from biological, medical and atmospheric science move to incorporate isotope measurements in their research programs, and as earth scientists already using isotope measurements exploit the new possibilities afforded to them.

Isotopic Evidence for Methane Formation and Decomposition in Marine and Freshwater Environments

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The recent development of the stable carbon isotope technique on nanoliter quantities of methane has been applied for the first time to trace the fate of methane in two different water bodies. Samples have been collected with Niskin bottles at several depth profiles in the water column: During the cruise So 80 B (R/V Sonne) in August 1992 in the Eastern Pacific (21 °S) above the tectonically active spreading ridge of the East Pacific Rise (EPR), where hot and gas enriched water enters the ocean and, in June 1993 during a cruise on Lake Constance (R/V Tienemann), a large freshwater resource in South Germany.

Dissolved gases have been extracted from one litre of water immediately after sampling. Concentrations of methane (and for Lake Constance also of nitrogen, oxygen and carbon dioxide) have been determined. Stable carbon isotopes of methane were analysed in the BGR laboratory.

Based on the geochemical data, in the area of the EPR (max. depth 3300 m) three types of water have been differentiated: Near-surface waters have methane concentrations of about 50 nl/l (nanoliter CH_4/litre water) and $\delta^{13}C$-CH_4 is close to -50 ‰. In deep waters (below 250 m) without hydrothermal influence methane concentrations are ≤ 20 nl/l ("background" concentrations) with $-40 ‰ \leq \delta^{13}C$-$CH_4 \leq -30$ ‰. Deep water, influenced by the hydrothermal input, contains CH_4 > 50 nl/l with $-40 ‰ \leq \delta^{13}C$-$CH_4 \leq -30$ ‰.

The preliminary interpretation is that the surface water is nearly in equilibrium with the atmospheric methane (ca. 50 nl/l). This methane is degraded (by bacteria?) in the sea-water down to background concentration levels. Methane from the local hydrothermal water mixes with the background methane in the layered water. Hydrothermal methane is only locally detectable but does not reach the surface. Based on our data, we conclude that at the time of investigation the Pacific water in the survey area is not considered to be a source for atmospheric methane, although there is input of hydrothermal methane into the bottom water, and in situ enrichment of surface water relative to atmospheric equilibrium conditions may not be excluded for the whole survey area.

Lake Constance (max. water depth ca. 250 m) represents a quite different hydrological and geochemical setting. Methane concentrations range from very low (~20 nl/l) values in the deep water to very high (~3000 nl/l) values at the surface. Isotope data is about $-25 ‰ \leq \delta^{13}C$-$CH_4 \leq -60$ ‰. Although in many areas of the lake the bottom sediments are very rich in methane, only minor contributions of this methane, if at all, into the water column can be recognised.

According to the common interpretation of isotope data, methane in surface waters of Lake Constance has a bacterial signature. We assume that methane generation takes place in these well oxygenated surface waters. In contrast to the area of the EPR, surface waters of Lake Constance are highly enriched in methane compared to equilibrium with the atmosphere. The pathway of methane formation and magnitude of methane flux into the air will be subject of future investigations, in which the isotope technique of small methane quantities may be a helpful tool.

Stable Carbon Isotopes on Methane in Nanoliter Quantities

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Methane is one of the trace gases which is thought to influence the global climate. Carbon isotope ratios have often been used to trace the methane in the soil, the hydrosphere and the atmosphere. Investigating the methane in the ocean water column, e.g. mostly few liters of water are available for gas extraction yielding only some nanoliters of methane for stable carbon isotope ratio determination. Therefore, an online GCIRMS-system (gas chromatography isotope ratio mass spectrometry) has been established to analyse those small sample quantities.

The main part of the unit is the MAT 252 mass spectrometer that is connected with a separate gas chromatograph and a combustion oven. A packed column (2 m in length, 1/8" in diameter, Porapak Q, on-column LN_2 cold trap) is used in the GC at 60 ^{o}C. Helium carries the sample through a cold trap (dry ice temperature) and a split system into the oven (CuO and Pt) where methane is converted into carbon dioxide. The CO_2 is transferred by He gas, supported by the pressure difference between the oven and the mass spectrometer, through a split system into the ion source. Data on the ion intensities at the three collectors (masses 44, 45, 46) are monitored and stored in a computer. For the very small signals, a software has been developed at BGR, used for peak detection, peak integration, and calculation of ratios and δ-values.

For analysis, each sample is injected via a syringe and is cryogenically focused on the column *prior to separation, combustion, and analysis. Although CH_4 and CO_2 in a sample often have* drastically different concentrations (e.g. air), they can be monitored in the same run due to the variable split system. Turnover time for one sample is less then 10 minutes and enables analysis of several samples within one GC-trace.

For calibration relative to PDB, known reference gases are repeatedly analysed, which have similar low methane concentrations as the samples. If methane concentration is in the range of the atmosphere, injected sample volume at present is about 2 ml, but may be adjusted to the actual samples. Due to the different splits, the amount of CO_2 (from the combusted methane) entering the ion source is less then 50 pmol.

Long term reproducibility of $\delta^{13}C$-CH_4 is below ± 1 ‰ (1σ). Daily reference analyses are often in the range below ± 0.5 ‰. Repeated analyses of collected ambient air (2 ml) were accurate to about ± 0.6 to ± 0.7 ‰.

Although the GCIRMS line generates data which are useful studying methane in the water column (applications will be presented), several parts of the whole system (split ratio, sample inlet system, international and laboratory reference gases) will be improved for better data reproducibility, better accuracy of the calibration on the PDB-scale, and reduction of sample size. Also, improvement of data handling could minimise total turnover time and help to reduce or avoid numerical errors.

MIXING AND DILUTION OF BRINES, BEREA SANDSTONE, OHIO; CHEMICAL AND ISOTOPIC EVIDENCE

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The Berea Sandstone (Late Devonian to Early Mississippian) underlies eastern Ohio at depths ranging from zero in the central part of the state to more than 670 meters in southeastern Ohio. The thickness of the formation ranges from 25 m or less in northern Ohio to about 10 m or less in the southeastern part of the state. The sandstone is fine to medium grained and is composed primarily of quartz (92-99.9%), K-feldspar (0.1-0.4%) and plagioclase (0.1-1.3%) grains. The cement consists of quartz with up to about 5% calcite, primarily at the base, and in thin layers as well as rare concretions. The Berea Sandstone is an important producer of natural gas and petroleum in Ohio.

The concentrations of major cations and anions of brines in the Berea Sandstone vary regionally and suggest that brines having elevated concentrations of Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, Br^- and I^- have entered this reservoir from the east. In view of the unreactive character of the quartz-sandstone reservoir, the regional variations in the concentrations of these ions are probably the result of mixing of two or more brines with concurrent dilution by meteoric water from the surface. Resolution of the brines into two components indicates that component A has elevated concentrations of Na^+, Mg^{2+}, and Cl^-, whereas component B is enriched in K^+, Ca^{2+}, and Ba^{2+}.

The $^{87}Sr/^{86}Sr$ ratios of most of the brines range from 0.711421±11 to 0.714570±6 with one sample at 0.720455±9, compared 0.710242±12 for NBS 987. The $^{87}Sr/^{86}Sr$ ratios increase from west to east indicating that the brine that invaded the Berea Sandstone from the east is enriched in radiogenic ^{87}Sr. A plot of $^{87}Sr/^{86}Sr$ vs 1/Sr forms a straight line after the Sr concentrations were corrected for dilution. The mixing equation yields the $^{87}Sr/^{86}Sr$ ratios for the brine components based on their average extrapolated Sr concentrations: Brine A, Sr = 346±11 mg/L, $^{87}Sr/^{86}Sr$ = 0.723; Brine B, Sr = 455±23 mg/L, $^{87}Sr/^{86}Sr$ = 0.7084. The $^{87}Sr/^{86}Sr$ ratio of component B is compatible with that of seawater during Late Devonian/Early Carboniferous time.

The $\delta^{18}O$ (SMOW) values of the brines range from -4.5‰ to -1.4‰ compared to $\delta^{18}O$ = -8.0‰ for modern meteoric water in Ohio. The $\delta^{18}O$ values of the brines, corrected for dilution with meteoric water, range from -1.6 to +1.2‰ with one anomalous brine at $\delta^{18}O$ = +2.15‰, $^{87}Sr/^{86}Sr$ = 0.720455. The average $\delta^{18}O$ value of the brines, after correction for dilution and excluding one anomalous sample, is -0.50±0.25‰.

This interpretation indicates that the chemical compositions and $^{87}Sr/^{86}Sr$ ratios of the brines can be understood in terms of mixing of two brine components with concurrent or subsequent dilution. However, the $\delta^{18}O$ values of the undiluted brines are not resolvable into components.

Stable isotopes (H, O, C): Generation and migration of hydrocarbons in evaporites (North Caucasus salt deposits as example)

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Most of the investigators consider a presence of salt-bearing horizons in a sedimentary sequence as a favorable factor for accumulation of hydrocarbon accumulations and their preservation during geological periods of time.

In North Caucasus hydrocarbon-bearing basin the Upper Jurassic saltairs are located in two depressions - Chernolessky depression and Kubansky foredeep. The evaporites are represented here by gypsum, anhydrite, rock salt and chloride-calcium brines. There is a unique circumstance that the Upper Jurassic salt-bearing formation is crossed by drillholes to the depth of 6 km with formation temperatures up to 250°.

Separate hydrocarbon accumulations are discovered through all the section of salt-bearing formation, but their bulk is associated with undersalt and oversalt deposits of Chernolessky depression and undersalt deposits of Kubansky foredeep (Fedorov, 1981; 1981; 1986).

Drilling of wells is extremly difficult because of anomalous high formation pressure (Fedorov, 1986).

Investigation of stable isotopes of hydrogen and oxygen of underground waters and carbon of oil was conditioned by a necessity to get an impression about generating potentiality of salt-bearing deposits, principal possibility and mechanism of hydrocarbon migration through the salt formation and for prognostic evaluation of prospectiveness for great hydrocarbon accumulations. Together with isotopic determinations there were realized investigations of organic matter in various salt-bearing rocks and gas-liquid inclusions of rock salt, as well as of oils, underground waters and brines.

In a result of held investigations a geochemical scheme generation and migration of liquid and gas hydrocarbons in the areal of the Upper Jurassic evaporitic formation, principal conclusions of which will be explained in the presentation.

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LATE DIAGENESIS AND THERMAL HISTORY OF THE MIDDLE ORDOVICIAN ST. PETER SANDSTONE, MICHIGAN BASIN: SOME EVIDENCE FROM ILLITE K/Ar AGES AND $^{18}O/^{16}O$ RATIOS.

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The Middle Ordovician St. Peter sandstone reservoirs occur throughout the central Michigan Basin at depths ranging from 1.5 to 3.5 km and have been intensely diagenetically altered. The latest diagenetic cements include burial dolomite and pervasive microcrystalline illite and chlorite. The clay cement commonly occurs in secondary porosity developped at the expense of previously formed burial dolomite and is postulated to have preceded hydrocarbon emplacement.

A K/Ar and $^{18}O/^{16}O$ study of the fine-grained authigenic illite of 25 samples from 16 wells mainly located in the central part of the basin was carried out. The purity of the samples was checked by use of XRD and TEM techniques as well as by assessing internal consistency of the data. K/Ar ages range from 369 to 322 Ma (average = 344 ±11 Ma) and $\delta^{18}O$ values range from 12.7 to 17.1 ‰ SMOW (average = 14.8 ±1.3 ‰).

These results indicate that the regionally significant episode of clay cementation occurred during Late Devonian-Mississippian times. Paleodepths of illitization were estimated on the basis on detailed burial reconstructions for each well and K/Ar ages. They vary between 1.6 and 1.8 km for two wells located along the edge of the basin and from about 2.4 to 3.2 km for a majority of wells situated in the central basin. Two-phase aqueous fluid inclusions located in a single crystal of burial dolomite from a central well yielded homogeneization temperatures ranging from 90 to 150°C. This and other evidence suggest that at least some of the fluid inclusions in the dolomite have been reequilibrated during burial. High Th values (140-150°C) may therefore be more representative of maximum burial conditions (about 4 km) in the central basin. Combined with the K/Ar ages and paleodepth estimates, these results indicate the existence of elevated geothermal gradients, i.e., greater than 30°C/km, in the Michigan basin in the Late Paleozoic. Combined with the illite $\delta^{18}O$ values they indicate the involvement of ^{18}O-rich fluids in late diagenetic cementation.

The variations in the K/Ar ages and, to a greater extent, in the $\delta^{18}O$ values ought to be significant. K/Ar ages and $\delta^{18}O$ values are not correlated to either present depths of the samples or reconstructed paleodepths of illitization. They are, however, correlated to one another, with $\delta^{18}O$ values increasing with increasing ages. In addition to purity checks, age and geological considerations indicate that, for the most part if not all, the latter correlation is unlikely to represent two-component mixing between detrital and diagenetic illite. Observed variations in the age and ^{18}O data must therefore represent actual variations in the conditions of illitization from well to well. TEM examination of many illite samples showed the existence of at least two distinct types of authigenic morphologies, *i.e.*, plates and laths. It is conceivable that different morphologies represent distinct generations of illite. Variations in the data may therefore reflect two or more episodes of illitization over a 40-50 Ma period of time. In addition, K/Ar ages of the illite cement tend to be younger, and $\delta^{18}O$ values lower, in wells located along the North-South branch of the buried Precambrian rift. Because the $\delta^{18}O$ values of diagenetic quartz overgrowths formed earlier in the diagenetic sequence exhibit a similar pattern, this geographical zonation may be significant. The range in illite $\delta^{18}O$ values is best explained as reflecting primarily a temperature effect rather a variation in the fluid isotopic composition. Thus, the part of the central Michigan basin located above the presumably highly fractured basement rift may have been characterized by abnormally high thermal regimes.

MEASUREMENT OF INTRACRYSTALLINE FRACTIONATION OF OXYGEN ISOTOPES BETWEEN HYDROXYL AND NON-HYDROXYL SITES IN KAOLINITE BY THERMAL DEHYDROXYLATION

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Thermal dehydroxylation was used to measure the intracrystalline fractionation of oxygen isotopes between hydroxyl and non-hydroxyl sites in kaolinite. Experiments were first performed on a well characterized kaolinite as well as on reference samples of gibbsite and brucite in order to test the validity of the approach. Similar experiments were then conducted on a suite of kaolinites and dickites of variable origin. Although further refinement and testing are required our results suggest that the thermal dehydroxylation approach may be suitable for determining the isotopic ratio of OH groups in fine-grained (<1 µm) kaolinite.

Several aliquots of a fine-grained (<1 µm) kaolinite from Macon, GA, were dehydroxylated *in vacuo* by heating with a resistance furnace. The evolved water was frozen with liquid N_2 as dehydroxylation proceeded, minimizing opportunity for isotopic exchange between water and dehydroxylated residue. Various combinations of heating procedures (single-step, two-step and multi-step), heating rates (about 1°C/min to 200°C/min), and ultimate temperatures (from 500°C to 1000°C) were investigated. Dehydroxylation experiments performed using a two-step or a multi-step procedure yielded inconsistent results suggesting significant, rate-dependent isotopic fractionation and/or isotopic exchange between different oxygen sites. In contrast, measured $\delta^{18}O$ values of both the liberated water and the dehydroxylated residue are very consistent, within about 1 per mil, over a wide range of target temperatures and heating rates when dehydroxylation is performed in a single-step fashion. At temperatures between 550 and 850°C the $\delta^{18}O_{water}$ values average 6.5 ±0.3 per mil and the $\delta^{18}O_{residue}$ values 26.0 ±0.1 per mil. The $\delta^{18}O$ value of the bulk kaolinite is 21.7 ±0.2 per mil.

The results of similar single-step dehydroxylation experiments performed on brucite and gibbsite indicate that, 1) dehydroxylation of brucite, which follows a single-reaction pathway similar to kaolinite, occurs without any significant fractionation, and 2) gibbsite dehydroxylation occurs with substantial and variable isotopic fractionation, probably related to its complex multi-reaction pathway (formation of intermediate boehmite). Because brucite and kaolinite have similar dehydroxylation reactions, these results suggest that the oxygen liberated as H_2O during single-step thermal dehydroxylation of the <1 µm kaolinite may be unfractionated OH oxygen. The average $\delta^{18}O_{water}$ of 6.5 per mil may therefore be considered as representative of the isotopic composition of the OH groups. Alternatively, this constant value would have to represent a constant kinetic fractionation which seems unrealistic.

A coarser size fraction (1-10 µm) of the kaolinite from Macon and a series of four kaolinites and two dickites of weathering and hydrothermal origin were investigated under identical dehydroxylation conditions. The 1-10 µm size fraction of the Macon kaolinite yielded progressively increasing $\delta^{18}O_{water}$ values with increasing dehydroxylation temperatures. A marked temperature dependence of variable magnitude was also observed for all but one of the other kaolinites and dickites investigated. Detailed examination of the particle size distribution of these kaolinites/dickites revealed that, 1) they are characterized by particle sizes coarser than the <1 µm kaolinite by one to three orders of magnitude, and 2) they may exhibit bimodal or polymodal size distributions. These results suggest that the observed temperature dependence may be related to the coarse grain size of these samples. It is well known that diffusion of dehydroxylation water is retarded in coarse-grained kaolinite. We therefore postulate that oxygen exchange during diffusion of the water through large particles may be responsible for all or part of the inconsistencies in the $\delta^{18}O_{water}$ values measured for the coarse grained (>1 µm) kaolinites and dickites.

EARLY AND LATE DIAGENETIC ILLITES FROM THE MIDDLE RIPHEAN DEBENGDA FORMATION, NORTHERN SIBERIA: THE Rb-Sr EVIDENCE

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Clay fractions of the shales of the Middle Riphean Debengda Formation, Olenek Uplift, Northern Siberia, were studied by the Rb-Sr method. The studied rocks, exposed within a stable cratonic area, remain nearly flat lying, and they are essentially unmetamorphosed. Color indices of the organic-walled microfossils from different horizons of the Debengda Formation signal very mild thermal history of the rocks while the thickness analysis of the post-Debengda Precambrian and Phanerozoic deposits of the area suggests that the studied rocks have never been buried deeper than 4.5 km.

Two samples of shale have been crushed and the <5 μm fraction was separated by means of ordinary technique. Then this fraction was separated into six (<0.1, 0.1-0.2, 0.2-0.3. 0.3-0.6, 0.6-2 and 2-5 μm) subfractions (SFs) using centrifugation and ultrafiltration. The three coarser SFs represent up to 80-85% of the total weight of the sample (ca. 25-30% each).

The XRD data reveal that the Al-Mg illite-smectite is the dominant mineral phase in all SFs and chlorite content in all but the 2-5 μm SF is under 5%; the latter SF consists of almost equal amounts of illite, chlorite and quartz. The illite crystallinity indices vary in the range of 1.3-1.5° $\Delta 2\theta$ and tend to decrease in finer SFs. The diffractional study demonstrated that 1M-1Md illite dominated the SFs smaller than 0.2 μm and 1Md illite prevails in the rest of the SFs.

Leaching with 1N ammonium acetate and Rb-Sr analysis of the untreated fractions, leachates, and residues make possible to fit Rb-Sr "leachochron" to each of these SFs and determine its apparent age and relevant $^{87}Sr/^{86}Sr$ initial ratio. With the size of particles decreasing from 0.6-2 μm to <0.1 μm, proportion of the leached Sr smoothly increased from 46.8-54.1% to 65.7-73.0% and the $^{87}Rb/^{86}Sr$ ratio in the residues increases from 9.0 to 16.1-18.1 in both studied samples. The apparent Rb-Sr age values unidirectionally decrease from 1212-1234 Ma for the 0.6-2 μm SF to 1040 Ma for the <0.1 μm SF, while the apparent $^{87}Sr/^{86}Sr$ initial ratios decrease from 0.7143 to 0.7134 in one sample and from 0.7132 to 0.7126 in the other.

All the evidences taken together indicate that studied SFs consist of two different generations of authigenic illite and contain them in various proportions. The first generation (1Md illite), with a lower Rb/Sr ratio, dominates the 0.6-2 μm SF and the second generation (1M-1Md illite), having a higher Rb/Sr ratio, is most abundant in the <0.1 μm SF. The intermediate (0.1-0.6 μm) SFs represent two-component mixtures of these end members of different age and hence their apparent Rb-Sr ages are meaningless. The apparent age of the 2-5 μm SF seems to be also meaningless because the two-component relations are drastically disrupted in this SF.

Apparent Rb-Sr ages (1212-1234 Ma) of the 0.6-2 μm SF represented by 1Md illite are very close to the K-Ar and Rb-Sr isochron ages (1265 and 1245 Ma respectively) of glauconite from the underlying part of the Debengda Formation. A small discrepancy between isotopic ages of this clay fraction and glauconite may be attributed to the existing difference in the stratigraphic position of the relevant samples, or to a later formation of authigenic illite. In any case, the above isotopic ages are in agreement with the stratigraphic age of the Debengda Formation, defined by paleontological data and correlation with the Siberian hypostratotype of the Riphean. Thus, they can be considered as the early diagenesis age. The age (1040 Ma) of the second illite generation represented by 1M-1Md illite corresponds to a later event, presumably, to late diagenesis (catagenesis). Established differences in the apparent $^{87}Sr/^{86}Sr$ ratios in the different and heterochronous illite SFs testify to a limited migration of the Sr in course of the above processes.

Poster

THE CONTRIBUTION OF TIN-LEAD CAPSULES AS A SOURCE OF LEAD IN WINE

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The lead isotope fingerprinting method has been used to determine whether soluble lead compounds produced by reaction of wine with tin-lead capsules are drawn back through and/or around corks to give an apparently elevated lead content in wine.

Lead isotope abundances and precise lead concentrations have been measured in wines, corks and capsules for over 50 bottles of mainly Australian and a few German wines. To minimize variables such as soil type and winemaking procedures, most samples are from the one vineyard covering a 15 year period. The sample population is biased towards a "worst-case" scenario in choosing a larger number of bottles with significant corrosion and possible cork damage.

Lead contents and isotopic values of the wine and corks are critically dependent on sampling procedures, so that for example, higher lead contents are recorded for decanted samples which had limited cleaning of the bottle neck and cork.

Lead contents of the Australian wines are generally low in the range of 20 to 60 µg/L. The lead isotope values are uniform for separate bottlings within a vintage but show variations both between bottlings of the same vintage; the variation between vintages are attributed to winemaking procedures.

When sampled rigorously, we find no correlation between the lead isotope values in the wine and capsules nor a correlation with isotope values and the degree of capsule corrosion. Furthermore, there is little difference in the isotopic values of wine from lead-capsuled and uncapsuled (or plastic capsuled) bottles of the same vintage. These results provide strong evidence that there is no migration of lead corrosion products back into the wine.

Cork profiles based on analyses of the top, middle and bottom of corks are complex depending on the methods of cork extraction and its preparation for analysis. With extraction by wine freezing and removal of the "rind", there is no evidence for lead migration through the cork. Limited lead migration over a distance of about 2 mm in the top of the corks is detectable in bottles whose capsules are severely corroded. Similarly, in corks with very low levels of lead (<0.2 mg/kg), the lead in the bottom 1-2 mm may equilibrate in time with that in the wine.

To minimize lead ingestion it is recommended that if the capsule exhibits moderate to severe corrosion, the top of the bottle and cork be vigorously scrubbed and rinsed with water prior to corkage and that the lower part of the cork remain unpierced.

If the cork is in good condition, lead in wine from capsule corrosion is not a problem.

SOURCE AND PATHWAYS OF LEAD IN HUMANS FROM THE BROKEN HILL MINING COMMUNITY

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To assist in recommendations for the most suitable lead abatement policies in Broken Hill, knowledge of the sources and pathways of the lead into humans is critical. We have approached these problems using the lead isotope fingerprinting method, combined with mineral speciation and "bioavailability" tests, approaches adopted from those applied to mineral exploration.

High precision lead isotope ratios and lead contents were measured by thermal ionisation mass spectrometry on biological samples (blood, urine, teeth) and environmental samples from 27 families, encompassing 60 children, 41 female adults and 17 male adults. Environmental samples analysed (not from every household) included soils, gutter sweepings, ceiling dust, vacuum cleaner dust, long-term dust, surface dust wipes, external and internal air, food, water, and gasoline.

Children have been identified using lead isotopes, complemented with knowledge of geographical location and personal details, with dominant contributions to blood lead (PbB) of lead from an orebody, gasoline or paint source. Of 28 children with PbB >15 µg/dL, ~30% have more than 50% of their PbB from sources other than orebody lead. Female adults generally have low PbB, <10 µg/dL, and the source of their lead is attributed to air (gasoline, orebody), food and water. The source of lead in male adults can be usually correlated with their occupation, depending on whether it is related to high-risk activities such as mining (dominantly orebody lead) or service stations (gasoline lead) or "non-exposed". Knowledge of the occupation and lead isotope composition in the father's blood is an important indicator of lead pathways. Other potential sources of lead such as food and water have lead contents too low to be significant contributors to PbB in most children.

Scanning Electron Microscopy (EDX analyses) identified the most common lead species in soils and dusts to be composed of as a complex Pb Fe Mn Ca Al Si O material with rare galena in houses close to the central mining activity. These lead complexes are quite different from other mining communities where the lead may be in less soluble forms such as pyromorphite, or encapsulated in less soluble anglesite, pyrite or quartz. Approximations of "bioavailability" (more correctly, solubility) were made by leaching, with 0.1M HCl for 2 hours at 37°C, bulk (unsized) and a 'critical' size fraction of -53+38 µM. The 0.1M HCl extracts 33 - 61% (mean 47±10%, N=7) of the total leachable lead from gutter sweepings, from 41 - 84% (mean 60±10%, N=10) from soils, and 17 - >100% (mean 47±38%, N=5) from vacuum cleaner dusts. Thus a Broken Hill child ingesting soil ('dirt') and dust at the currently suggested amounts of ~100 mg/day, can readily account for the elevated PbB's compared with many other mining communities. Based on these investigations it is possible to construct a flow sheet of sources and pathways for the lead into humans at Broken Hill on which to base correct remedial actions.

STABLE ISOTOPE STUDY OF GRAPHITE DEPOSITS IN THE BOHEMIAN MASSIF

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The isotopic study was carried out on several graphite deposits located in the so called Varied Groups of Moldanubicum, Moravicum and Silesicum in the Bohemian Massif. The lithologically varied complexes are formed by paragneisses, mica schists, crystalline limestones, dolomites, calc silicate rocks and metabasites. All rocks were affected by metamorphism of amphibolite facies.

Carbon isotopic composition of graphite and carbonate from marbles with high content of graphite were used for determination of metamorphic temperatures. The wide range of "isotopic" temperatures (from 470 to 610°C) indicates that isotopic equilibrium between the above species was not attained. The $\delta^{13}C$ values of marbles and dolomites without graphitic admixture are in the range which is typical of marine sedimentary limestones. However, the oxygen isotopic composition of these marbles was affected by metamorphic processes.

Sulphur isotopic composition of sulphides from different types of rocks was also determined. Considering that sulphates are absent in these rock complexes it is possible to assume that $\delta^{34}S$ values of sulphides were affected by metamorphic processes only minimally. This implies that sulphur isotope data of sulphides from high-grade metamorphic terranes are applicable to a reconstruction of the pre-metamorphic environment. The $\delta^{34}S$ values of most sulphides from graphitic gneisses and mica-schists vary between -6 and $+8^{0}/_{00}$ and give evidence that these sulphides were formed from hydrogen sulphide which originated in anoxic environment, probably in shallow water lagoons with limited supply of sulphate and reactive iron. The isotopic composition of sulphidic sulphur in other metasediments ranges within a broad interval from -8 to $+28^{0}/_{00}$, which reflects a surplus of reactive iron in the system. The $\delta^{34}S$ values from metabasites range from 0 to $+32^{0}/_{00}$ and it is possible to assume that these rocks were contaminated by sulphur from the surrounding metasediments.

Deduction of diagenetic reaction mechanisms and transport patterns from isotope geochemistry.

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Sr isotope data from residual salts from regularly spaced core samples is a very useful basis for the diagenetic interpretation of sedimentologic, petrographic, thermometric and isotopic data from petroleum bearing sedimentary sequences. Genetic relations between pore waters from different stratigraphic levels, structural blocks and depths of burial from Devonian-Tertiary North Sea reservoirs have been established through such integrated studies of both sandstones and mudrocks. Isotope systematics has further been used to evaluate the advancement of diagenetic recrystallization of clays and carbonates, and to identify important pH buffers and paths of mass transfer.

Comparison of $^{87}Sr/^{86}Sr$ values from a large database (more than 2000 analyses) of present day pore waters (residual salts) and diagenetic minerals show that both stratigraphic effects related to depositional environment, weathering and early diagenesis, and effects related to deep burial diagenesis can be recognized. Middle and Lower Jurassic reservoirs buried to more than 3-3.5 km show pronounced effects of diagenetic recrystallization, leading to very high $^{87}Sr/^{86}Sr$ ratios (>>0.713) in sandstone and mudrock pore waters. Upper Jurassic, Triassic and Devonian sequences do not show these elevated $^{87}Sr/^{86}Sr$ ratios, even when deeply buried. Extensive removal of cations during weathering and early diagenesis is probably the main reason for the apparent higher reactivity during later deep burial for these Middle/Lower Jurassic sediments, compared to older and younger intervals.

Oxygen isotopes in Jurassic mudrock kaolinites and illite-smectites appear to be very close to equilibrium with the present day pore waters at depths from 1.5 to 4.5 km in the North Sea Viking Graben. Rb-Sr age determinations of illite/smectite separates from theses mudrocks also strongly support the near-complete equilibration with the present environment. Fine grained carbonate cements in the mudrock matrix are in most cases not in oxygen isotopic equilibrium with the present day pore water. A very high initial content of kaolinite in Lower and Middle Jurassic mudrocks is to a large extent of detrital origin. We interpret this kaolinite to have undergone continuous recrystallization by crystal ripening during burial. Upper Jurassic (Draupne) mudrocks are more rich in illite/smectite, relative to kaolinite, than the Lower and Middle Jurassic mudrocks, but isotope data indicate the same type of continuous clay recrystallization with burial.

The composition of intra-reservoir mudrocks in Brent and Statfjord reservoirs is generally similar to the kaolinite rich thicker external Dunlin mudrocks, but the importance for reservoir quality may be different, because of the internal position of the former. Evolution of clay mineral crystal size populations by crystal ripening may lead to net transport of clay components by diffusion to interbedded sandstones. This may lead to effective occlusion of sandstone pore spaces by authigenic clays formed by growth over long time periods (and increasing temperature), consistent with the observed 1-3 ‰ higher $\delta^{18}O$ values in sandstone kaolinites compared with nearby mudrock kaolinites. The largest crystals in the mudrocks will still be unstable with respect to much larger crystals in sandstones. This will lead to a closer approach to isotopic equilibrium at all times in the mudrocks, consistent with $\delta^{18}O$ and Rb-Sr results.

The pH of thin intra-reservoir mudrock pore waters will mainly be controlled by the surrounding sandstone system, and carbonates may therefore not be so effectively redistributed from internal mudrocks to sandstones. Intra-reservoir mudrock reactions appear to be very important for clay mineral cementation in originally relatively clean sandstone layers. Internal kaolinite rich mudrocks may also be important for secondary porosity development at great depths (>4 km), through the process of illitization of kaolinite. Mudrock layers rich in kaolinite may act as a sink for K^+, and consequently promote K-feldspar and mica dissolution in nearby sandstones.

Thicker kaolinite and organic rich mudrocks external to the reservoirs (like the Dunlin Group of the North Sea) may be important for carbonate dissolution, cementation, and development of secondary porosity in sandstones at all stages, because kaolinite buffered acidic pore waters rich in organic acids, may dissolve considerably larger quantities of carbonate ions than higher pH pore waters in equilibrium with mica, illite and feldspars in the reservoirs.

Using Sr isotopes of residual salts to monitor crossformational and large scale lateral transfer of Sr, deductions about the fluxes and transport paths of other important cations (and consequently anions) relevant to diagenetic predictive models appear to be possible.

Stable carbon and hydrogen isotope studies of natural gases from the Polish Flysch Carpathians

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Stable isotopic studies were undertaken to investigate the origin of 28 natural gases (free and dissolved in oils) from eastern and central parts of the Polish Flysch Carpathians.

The Polish Flysch Carpathians are located in the outer part of a young Alpine orogenic belt of nappe-thrust structures. The structures are composed of numerous complexes of sandstones and shales as much as 8 km total thick, ranging in age from Lower Cretaceous to Oligocene. The Polish sector of the Flysch Carpathians includes the following structural units: Magura, Fore-Magura, Grybow, Obidowa-Slopnice, Dukla, Silesian, Sub-Silesian, Skole and Stebnik.

The Polish Flysch Carpathians are one of the earliest areas of petroleum exploration and exploitation. The exploitation of oil started in 1854 and that of natural gas in 1921. Up to date, 68 oil fields and 15 gas fields have been discovered in this region.

The investigated gases are variable in both their molecular and isotopic composition. Geochemical indices and stable isotope ratios vary within the following ranges: gas wetness values $\left[C_{HC} = CH_4/(C_2H_6 + C_3H_8)\right]$ from 4 to 1145; methane $\delta^{13}C$ values from -65.6 °/oo to -34.2 °/oo; methane δD values from -207 °/oo to -151 °/oo; ethane $\delta^{13}C$ values from -47.2 °/oo to -26.2 °/oo and propane $\delta^{13}C$ values from -31.6 °/oo to -24.4 °/oo. These variable molecular and stable isotope values, in addition to geological conditions, allow the identification of three genetic types of natural gases: low-temperature thermogenic (associated), high-temperature thermogenic (non-associated) and bacterial.

Low-temperature thermogenic gas component was generated from the indigenous organic matter deposited in sediments of the Flysch Carpathians. High-temperature thermogenic gas component was very likely generated within the deepest section of flysch complex and also partly migrated from the Paleozoic-Mesozoic basement, an mixed with the indigenous flysch hydrocarbons.

Sporadically, bacterial gases are also encountered. Bacterial gases were generated within the flysch sediments and/or migrated from Miocene sediments of the Carpathian Foredeep.

Migration and mixing of the gases of different origins have commonly taken place within the flysch complex.

The Grenville-gold Connection and the Dating of Deformation

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Hydrothermal emplacement into transgressive faults and shear zones at high crustal levels is an integral part of the orogenic process yet direct evidence linking deep and shallow crustal processes are few. The Superior Province in Canada provides such an example. Here granulite grade mafic gneisses indicate episodes of dehydration, rehydration and ductile flow between 2660 - and 2585 Ma about 40 to 115 Ma after the cessation of volcanism in the nearby Abitibi greenstone belt. This episode of post accretion granulitization of the middle crust is matched in time by episodes of gold emplacement into active fault and shear zones at high crustal levels.

In this example the ages of faulting at high crustal levels are inferred by the ages of pre and post deformation gold emplacement deduced from U-Pb ages of titanite monazite and rutile. At Hemlo ages of 2670, 2640 and 2632 are given by titanite, monazite and rutile analyses for different ore zones. This ore is sheared so that deformation as young or younger than 2632 Ma is implied (Corfu 1989). Mineralization at Camflo mine (Jemielita, et al 1990) is dated at 2625 Ma by analyses of titanite and rutile in both vein and massive ore. Gold emplacement at 2599 Ma was determined by rutile analyses (Wong, et al 1991) at the Sigma mine where post-ore deformation is entirely absent. The youngest gold-related rutile is dated at 2585 Ma.

Examples of direct dating of deformation are provided by studies in the Grenville Front tectonic zone. Near North Bay progressively reset and new growth monazite indicate thrusting at 988±5 Ma whereas nearby post shear relaxation melts provide new growth zircons in an Archean host with ages of 987,987, 986 Ma (single tips). At two other localities titanite show variable degrees of resetting one at 977±12 Ma the other at 988±5 Ma. These sites are as much as about 1500 km apart. Post deformation relaxation melts in the Front on the Labrador Coast provide a surprising result with a 1630 Ma titanite age as if an older thrust has been uplifted during Grenville thrusting.

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Use of Stable Isotope Data to Monitor *In Situ* Processing of Oil Sands

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Although much bitumen from oil sand occurrences in northeastern Alberta has been processed by surface operations, the bulk of the deposits must be recovered by sub-surface mining. Because of high viscosity, heat must be applied to the reservoir to encourage flow of the bitumen. A variety of *in situ* techniques are employed. High-temperature water-steam mixtures (~300°C) may be injected over 2 or 3 months. After the reservoir is left to heat for a month, bitumen may be recovered from the injection well. Alternately, an injection well may be surrounded by recovery wells. *In situ* combustion is also employed utilizing some of the bitumen as fuel and injecting air and/or oxygen. In high temperature combustion regions, thermal cracking produces volatile gases and residual coke in addition to more desirable liquid fuel. Water may be also sequentially or co-injected into combustion drives.

Stable isotope data from either water or gasses are very useful in elucidating *in situ* processes. (Hallam *et al.*, 1988; Hutcheon *et al.*, 1990).

In simplistic terms, the bitumen has a $\delta^{13}C$ value near -30 ‰ whereas natural methane and carbonate cements in these sands have $\delta^{13}C$ values near -55 and 0 to +20 ‰, respectively. In steam drives, the $\delta^{13}C$ values of CO_2 increase towards 0 ‰ attesting to interaction of the fluids with carbonate cements whereas those for CH_4 remain near -55 ‰. In contrast, during combustion, the $\delta^{13}C$ values of CO_2 decrease towards -30 ‰ because of oxidation of bitumen whereas that of CH_4 increases up to higher than -40 ‰ because of cracking reactions.
The isotope data prove most useful when production wells surrounding an injection well are routinely monitored. In this way, subsurface movement of steam or combustion fronts can be mapped over time.

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Carbon Isotopic Composition of Methane in Crystalline Rocks of the Siljan Impact Structure - Sweden

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Two deep wells have been drilled in the crystalline rocks within the Siljan impact crater, central Sweden, which was formed 360 Ma ago. The objectives of the drillings were to explore for abiogenic deep mantle gas *in the fractured rocks, which consisted mainly of 1.75 - 1.65 Ga old granites. 0.7 - 1.0 Ga old dolerite* intrusions (sills and dykes) dissect the granites. The first well, Gravberg-1, was drilled on the rim of the transient crater and reached a depth of 6779 m (TVD) and the second well, Stenberg-1 drilled in the center of the crater, penetrated to a depth of 6529 m (TVD).

Hydrocarbons were *detected in both wells, in the drilling fluid and in sealed samples of cuttings.* The highest concentrations of methane were associated with the dolerite intrusions, 4500 µl/l of methane in the drilling fluid (Gravberg-1, 2652 m) and 1100 µg/kg methane in the sealed cuttings (Stenberg-1, 5953 m, headspace analysis). The dolerite methane constitutes up to 98 per cent of the total hydrocarbon gases. The *stable carbon isotopic ratios of the methane ($\delta^{13}C$: -5 and -15 o/oo) indicate an abiogenic origin of the* gas. The $\delta^{13}C$ values of the methane of sealed dolerite cuttings were a little less negative for Stenberg-1 well compared to those of the Gravberg-1 well, Fig. 1. This may due the fact that dolerite cuttings from the Stenberg-1 drilling were specifically collected and analysed, whereas the results from the Gravberg-1 well *(Fig. 1) are from cuttings of equidistant intervals, which may represent mixtures of dolerites and granites.* However, it should also be noted that the Stenberg-1 results were obtained from sealed samples of washed cuttings whereas those from Gravberg-1 were from unwashed cuttings. The amounts and relative abundances of methane released from cuttings by either acid desorbtion in a vacuum system or by ball mill crushing were *also distinctly higher for dolerite samples compared to those for granite samples.* Furthermore the methane of the dolerite samples were enriched in ^{13}C compared to those of the granite.

The methane associated with the dolerites may be primary magmatic (mantle) gas or a secondary product of post-magmatic dolerite alteration. Interaction of water with mafic and ultramafic rocks (e.g. serpentinization *process) may produce sufficiently reducing conditions* (a few f_{O2} units *below the* QMF buffer) to produce free hydrogen and, if carbon is present, methane.

The chemical and isotopic compositions of the hydrocarbons associated with the granites (Fig. 1) are distinctly different from those of the dolerites. Furthermore, the granite gases were also relatively rich in unsaturated hydrocarbons, *which are very unusual among natural thermogenic gases.* Therefore, it is likely that these hydrocarbons were formed as a result of a catalytical reaction e.g. a type of Fischer-Tropsch reaction, equation 1.

$$CO + H_2 \xrightarrow{iron/magnetite} CH_4 + C_nH_{2n+2} + C_nH_{2n} + H_2O \text{ (eq. 1)}$$

This catalytic reaction is known to produce saturated as well as unsaturated hydrocarbons.

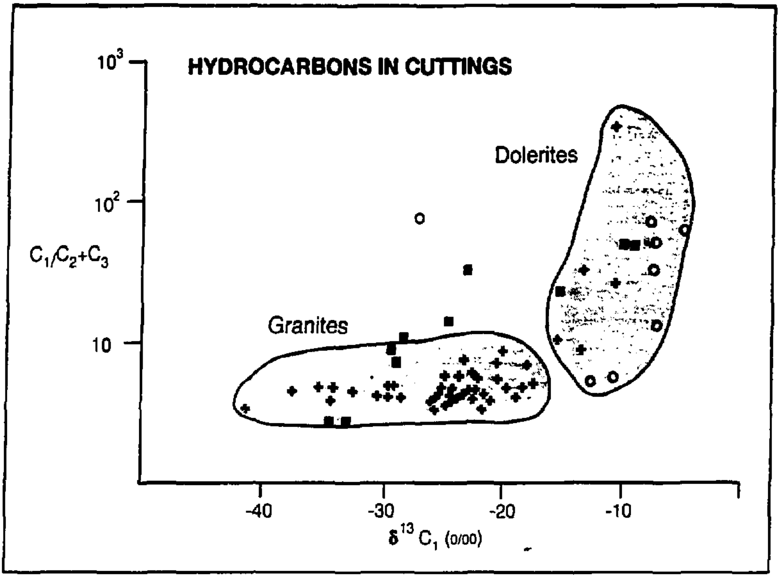

Fig. 1. Relation between chemical and isotopic composition of hydrocarbons, (+) desorbed, (■) headspace from Gravberg-1 and (○) headspace from Stenberg-1. The headspace data above the shaded area representing the granites were obtained for granites adjacent to dolerites.

Retention of Deposited Sulphate in Acid Forest Soils Determined by Sulphur Isotope and Mass Balances

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To quantify the impact of changing sulphur inputs on terrestrial and aquatic ecosystems, knowledge of sulphate transport from the soil surface to groundwater and associated biogeochemical transformations is essential. It is widely believed that, dependent upon the presence of other mobile anions, retention of SO_4^{2-} in the unsaturated zone can reduce the movement of acidifying cations and thus minimize stream acidification (Mitchell et al., 1992).

In this study, 75 cores (30 cm diam., 60 cm depth) from five German acid forest soils with total sulphur δ^{34}S-values near 0‰ were irrigated with sulphate solutions having a δ^{34}S-value of +28‰. Input-output balances were complemented by an inventory of different forms of soil sulphur and their isotope compositions. Since sulphur isotope discrimination during microbial and physicochemical sulphur transformations is small under aerated conditions (Krouse et al., 1991), the above difference in δ^{34}S-values is sufficent to isotopically trace the penetration and conversions of the irrigated sulphate. Not only could sulphur transformations in the soil be recognized but their dependence on sulphate deposition rates was quantified by using three different irrigation solutions.

After 20 months, the throughput of irrigation sulphate did not exceed 33 percent, although the mean transit time of the seepage water was of the order of only a few months. Examination of the soil sulphur pools and their δ^{34}S-values before and after irrigation showed, that added SO_4^{2-} was retained in the uppermost humic horizons dominantly as organic sulphur compounds and in the deeper mineral soil as inorganic sulphate. Independent of soil type and irrigation treatment, approximately two thirds of the retained sulphur was bound inorganically while one third was immobilized as organic sulphur. The high retention capacity as determined by direct measurements on soil and the low recovery of irrigation sulphate with the seepage water implies mean residence times for sulphur in the uppermost 60 cm of forest soils of the order of decades.

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Depositional and diagenetic $\delta^{34}S$ signatures in 2.0 Ga-old 'black shales': isotopic constraints for the sulphur source of ultramafic-hosted Ni-Cu sulphide ores, Pechenga, Russia.

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The Pechenga Ni-Cu sulphide ores are hosted by differentiated mafic-ultramafic gabbro-wehrlite bodies which are located within a 600-1,000 m thick 'black shale' formation named the Pil'guyarvi Sedimentary or 'Productive' Formation (PF). The gabbro-wehrlites are associated temporally and spatially with ferropicritic volcanics and NMORB-like tholeiitic basalts. The gabbro-wehrlites are co-magmatic (Predovsky et al., 1971) and coeval at ca. 2.0 Ga (Hanski & Smol'kin, 1989) with the ferropicrites. The ores are magmatic in origin and commonly situated on the bottom of the intrusions (Gorbunov,1968) or ferropicritic flows (Gorbunov et al., 1989).

From previous studies (Grinenko et al., 1967; Genkin et al., 1987; Akhmedov & Krupenik, 1990; Grinenko & Smol'kin, 1991; Hanski, 1992) it is known that the $\delta^{34}S$ of disseminated sulphides in the gabbro-wehrlite bodies varies from +5‰ to +9‰ (Fig. 1e, g, h, j, k, m). Ferropicritic flows are characterised by $\delta^{34}S$ of -0.2‰ to +7.1‰ (Fig. 1p, q). The $\delta^{34}S$ value of the Ni-Cu ores ranges from -3‰ to +8.5‰ (Fig. 1f, i, l, n, o). The reported $\delta^{34}S$ values of sedimentary sulphides in the PF spread from -5‰ to +21‰.

Sulphur source, timing and mode of formation of the Pechenga Ni-Cu ores have been subjects of discussion by several authors (Gorbunov, 1968; Grinenko et al., 1967; Stromov, 1985; Pushkarev et al., 1988; Grinenko & Smol'kin, 1991; Hanski, 1992). Previously proposed models considered either a predominantly mantle origin for the sulphur, a crustal origin, or a local sulphur source, the host 'black shales'.

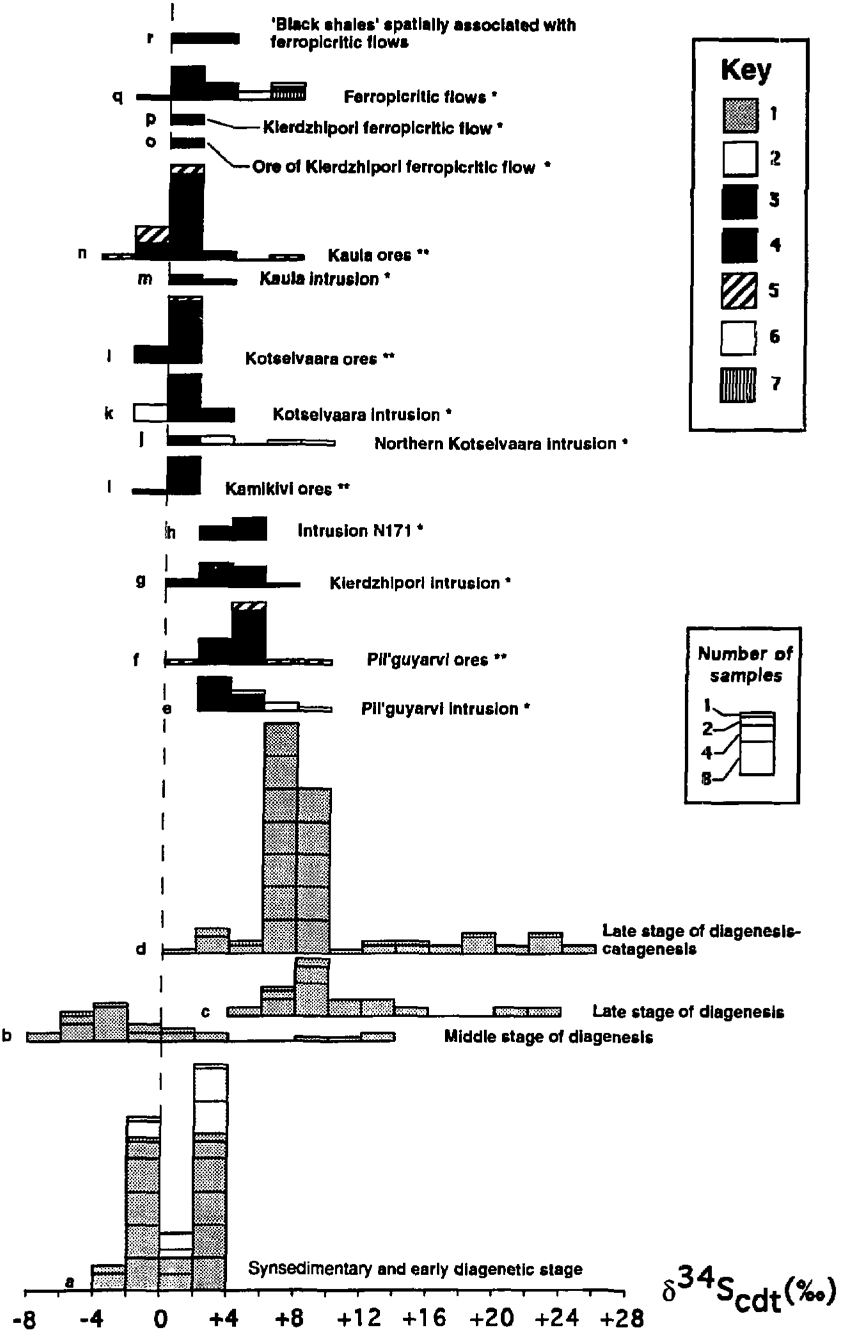
All the models discussed are based on the comparative bulk isotope geochemistry. This generally correct approach brought, in the Pechenga case, a number of uncertainties. This is because the sulphides of the host 'black shales' are represented by four temporal generations of pyrite and two generations of pyrrhotite. The mineral assemblages of the ultramafic rocks and ores are even more complicated. Within the 'black shale' sulphides, synsedimentary, early diagenetic, late diagenetic, catagenetic (next to metamorphic) and metamorphic sulphides are distinguished. The data obtained by the present authors show that sedimentary and early diagenetic sulphides represent a very tight $\delta^{34}S$ pattern with maxima between -2‰ +0‰ (Fig. 1a, r) and between +2‰++4‰ (Fig. 1a). They were probably formed in a rift 'black smoker'-like environment. The $\delta^{34}S$ values for sulphides of the middle stage of diagenesis (Fig. 1b) range from -8‰ to +14‰ with maxima between -2‰+-6‰. The late stage of diagenesis (Fig. 1c) and the catagenetic stage (Fig. 1d) produced sulphides which $\delta^{34}S$ spreads from 0‰ to +28‰ with maxima between +8‰÷+10‰ and between +6‰÷+10‰ respectively. The majority of sulphides are represented by the 'a', 'c' and 'd' patterns.

On the balance of evidence the present authors conclude that both barren (Fig. 1j, q) and ore-bearing (Fig. 1k, m, p) ferropicritic flows and their ores (Fig. 1i, l, n, o) are contaminated to ca. 25% by synsedimentary-early diagenetic sulphur of the PF with mean value between 0‰÷2‰. Both barren (Fig. 1h) and ore-bearing (Fig. 1e, g) intrusions and their ores (Fig. 1f) are contaminated to ca. 25-60% by the bulk of the PF sulphides with average $\delta^{34}S$ value between +4‰+6‰. The $\delta^{34}S$ of marginal sulphides of intrusions, flows and ore bodies was overprinted during the catagenetic stage with records up to +10‰.

Fig.1. The $\delta^{34}S$ patterns of sulphides representing the ultramafic intrusions, ferropicritic flows, Ni-Cu ores and 'black shales' of the PF, Pechenga, Russia..

1-sulphides of the PF; 2-synsedimentary sulphides of the PF from Akhmedov & Krupenik, 1990; 3-synsedimentary sulphides associated with ferropicritic flows; 4-disseminated sulphides of intrusions and ferropicritic flows, and ultramafic-hosted Ni-Cu ores; 5-sulphides of 'black shale'-hosted Ni-Cu ores; 6-sulphides from the lower margin of intrusions and ferropicritic flows; 7-sulphides from upper contact of ferropicritic flows.

* Data from Grinenko & Smol'kin (1991), ** and from Grinenko et al. (1967). The Kotselvaara and Kaula intrusions are considered in this study as ferropicritic flows.


r 'Black shales' spatially associated with ferropicritic flows
q Ferropicritic flows *
p Kierdzhipori ferropicritic flow *
o Ore of Kierdzhipori ferropicritic flow *
n Kaula ores **
m Kaula intrusion *
l Kotselvaara ores **
k Kotselvaara intrusion *
j Northern Kotselvaara intrusion *
i Kamikivi ores **
h Intrusion N171 *
g Kierdzhipori intrusion *
f Pil'guyarvi ores **
e Pil'guyarvi intrusion *
d Late stage of diagenesis-catagenesis
c Late stage of diagenesis
b Middle stage of diagenesis
a Synsedimentary and early diagenetic stage
Key
1
2
3
4
5
6
7
Number of samples
1
2
4
8
-8
-4
0
+4
+8
+12
+16
+20
+24
+28
$\delta^{34}S_{cdt}$(‰)

The C-isotope perturbation at the Permian/Triassic boundary: Evidence of a greenhouse overshoot?

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The faunal and floral extinction in the transition from the Permian to the Triassic is one of the major events in Phanerozoic Earth history. The extinction is manifested by an apparent isochronous shift in the $\delta^{13}C$ values of organic carbon from marine and nonmarine sections which mirrors that which has been detected in numerous carbonate sections around the world. This C-isotope shift offers a unique tool whereby it may be possible to calibrate biostratigraphic schemes based on both marine and nonmarine oganisms worldwide at the P/Tr and suggests C-isotope chemostratigraphy may thus be a useful correlation tool on the inter and intrabasinal scale across the world. Studies of organic carbon in whole-rock fine-grained sediments from Australian marine and nonmarine sedimentary basins have yielded $\delta^{13}C$ shifts of between 6-8 permil consistently within or close to the *Protohaploxypinus microcorpus* palynology zone. This isotope study was carried out on samples obtained from fully cored boreholes drilled to acertain stratigraphy and conventionally cored intervals from petroleum exploration wells. Basins studied, their interpreted paleoenvironment around the Permian/Triassic boundary, palynological control on the section and the size of the detected $\delta^{13}C$ shift are shown in the table below.

SECTION	**PALEO-ENVIRONMENT**	**PALYNOLOGICAL CONTROL**	**$\delta^{13}C_{PDB}$ SHIFT** ***Permian to Triassic***
Bonaparte Gulf Basin	Marine	Good	-24 to -32
Canning Basin	Marginal marine	Good	-24 to -32
Cooper Basin	Lacustrine	Moderate	-24 to -30
Bowen Basin	Fluvial/Lacustrine	Good	-24 to -30
Sydney Basin	Fluvial/Lacustrine	Moderate	-24 to -29

The nature of the isotope shifts at the Permian/Triassic boundary can be characterised as either gradual which is interpreted as indicating complete and representative section or sudden which is interpreted as representing incomplete or condensed section. The suddeness of the shift in the C-isotope profile of the Canning Basin section suggests it to be a disconformity or condensed section at the boundary.

The similarity in the isotope profiles suggests the role of atmospheric carbon dioxide is pivotal in the the equilibration of C-isotopes across a range of sedimentary environments. The shape of the C-isotope profile through the Late Permian and Early Triassic in the interpreted complete sections supports a model of palaeoclimate which suggests greenhouse warming as a major contributing cause to the extinction event at the Permian/Triassic boundary.

The Late Permian in Gondwana was characterised by glacial conditions with extensive *Glossopteris* forests and coal forming basins in a high relative sea-level environment.The abrupt transition to a warmer low sea-level stand in the earliest Triassic is enigmatic but may be explained by the following scenario.

1. Subduction rates might have declined globally as a result of the assembly of the Pangean supercontinent. This slowing may have been due primarily to slower rates of subduction as less dense continental crust subducted upon closure of oceanic basins. A lowered, gravitationally induced, momentum on the less dense continental crust subducting may have slowed the rate of subduction and hence reduced spreading rates at the mid oceanic ridge. This would have produced an overall increase in the depth of the ocean basins as the mid ocean ridge profile contracted due to increased cooling and density of the ocean floor more proximal to the ridge. A decrease in the total length of continental shelf would have occurred with continent amalgamation.

2. The fall in sea-level that should have occurred with deepening of the world's ocean basins was masked by transfer of water from continental reservoirs to the world's ocean and ocean thermal expansion. Warming was accomplished by an increase in flux of carbon as carbon dioxide to the atmosphere. The source of that carbon was oxidation of ^{13}C depleted carbon from continental margin and shelf sediments whenever sea-level fell. A cycle may have been established throughout the latest Permian whereby minor tectonically induced sea-level falls were followed by greenhouse induced sea-level rises. The rise in atmospheric CO_2 levels may be marked on the organic carbon $\delta^{13}C$ isotope profiles by a change from values of around -22 permil PDB in the earliest Late Permian to values of around -24 permil PDB in the latest Late Permian in both marine and terrestrial sections. The similarity of marine and nonmarine C-isotope profiles in this period is probably related to the increase in the flux of carbon to the atmosphere and provides evidence for an enhanced greenhouse effect in the latest Permian.
3. Approaching the P/Tr, transfer of water from terrestrial reserviors such lakes and melting ice sheets may have climaxed. Thermal expansion of the world's ocean may not have been able to keep pace with the tectonically induced deepening. Sea-level would have fallen exposing continental margin and shelf stores of ^{13}C depleted carbon to enhanced erosion and oxidation.

The latest Late Permian was marked by the decline in the Gondwanan wide *Glossopteris* forests which were characterised by high levels of lignin with high carbon preservation potential. Furthermore the great inland Gondwanan lakes and ice sheets disappeared. The world's latitudinal thermal gradient was reduced. Clear evidence of continental ice is lacking in high latitude Latest Permian southern Gondwana. With the consequent reduction in thermohaline circulation of the ocean and its nutrient recycling ability which might be expected to occur with decreased latitudinal thermal gradient, ocean surface productivity may have declined. Continental shelves already reduced in area by the assembly of Pangea would have been subaerially exposed to further reduce ocean productivity while enhancing carbon-rich sediment erosion and oxidation. An increase in the organic load from the terrestrial environment to the continental shelves might have led to dysaerobic, low dissolved oxygen, conditions resulting in the deposition of ^{34}S-depleted sulfides produced by bacterial breakdown of sulfates and extensive shelf faunal extinctions. Reef formation on shelf areas was suppressed during the Early Triassic. A warmer enviroment extending to the polar regions may have led to the release of potentially huge volumes of ^{13}C-depleted methane stored in clathrates in tundra environments and polar continental shelves. The frequency of red bed deposits may have increased because organic productivity was at levels too low to prevent oxidation of the iron in sediments. Overall a situation may have developed throughout the latest Permian whereby positive feedback increased the levels of ^{13}C-depleted carbon that was oxidised in the environment while suppressing carbon storage. This carbon dioxide and associated methane from hydrates created a greenhouse world.

The greenhouse environment may have contributed to a loss of carbon sinks (coal forming environments, carbonate reefs, ocean surface productivity) and enhanced exposure of stored carbon to chemical weathering and oxidation (carbonate reef weathering, erosion of carbon rich sediments, breakdown of methane clathrates). Biodiversity declined in the earliest Triassic environment which was probably much changed from the earlier Late Permian.

These events may be marked on the organic carbon isotope profiles in the transition from the latest Permian to earliest Triassic by a gradual shift over some 300 000 - 600 000 years to C-isotope values of -29 to -32 permil. ^{13}C depleted values were maintained in organic carbon stored in sediments with minor fluctuation until the latest Middle to Early Triassic when there appears to be a return to heavier values around -24 permil. This time may be marked in the sediment record by:

1. Renewed coal deposition and preservation associated with the evolution and proliferation of the gymnosperms
2. Reef formation resumption
3. Decline in red bed deposition, and
4. Biodiversity recovery.

ENVIRONMENTAL ISOTOPES IN FLOOD FLOWS IN A MAJOR AUSTRALIAN RIVER

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The Murrumbidgee River in New South Wales is one of the major tributaries in the Murray-Darling Basin, which covers 1/7th of the Australian continent. The river is regulated by two upper catchment dams which supply summer irrigation flow. Winter flows are essentially unregulated once the dams are full. We describe detailed measurements of suspended solids concentrations, stable isotopes, lithogenic and anthropogenic radionuclides and mineral magnetic characteristics through a 1 in 12 and 1 in 5 year flood at point on the river below all tributary inputs. The two floods are contrasted by the source of flow; in the first flow was almost entirely through one of the storage reservoirs, in the second it was derived mainly from the catchment below the storages. The change of water source through the hydrograph is clearly illustrated by the stable isotope data, and the source of suspended solids is identified based on mineral magnetic data. The ratio of the fallout radionuclides ^{210}Pb and ^{137}Cs is used to show that sheet erosion is the mechanism responsible for delivering surface soil to the river, rather than channel bank collapse. It is concluded that tracer studies, including those based on environmental isotopes, have great potential in understanding the dynamics of flood transport in major rivers.

^{10}Be in a 5.4 Ma sequence of loess-fluvial-lacustrine sediments from North China: chronologic and climatic implications

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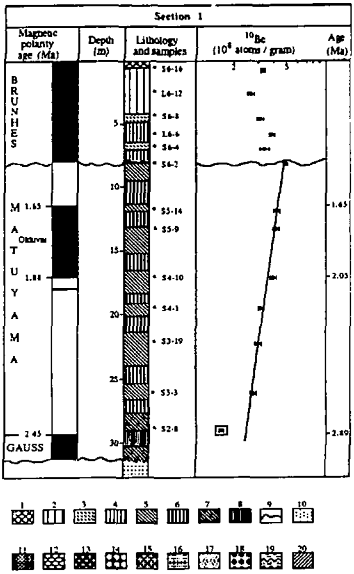
We present here results of ^{10}Be distribution in continental sediments from the Yushe basin (36° 50' N, 112° 40' E) which occupies the SE margin of the Loess Plateau of North China. The studied sediments include an eolian loess-paleosol section and a fluvial-lacustrine section with a minor talus in the lowermost part (Fig.1). This material offers an opportunity for evaluating the ^{10}Be dating and possible variations of regional signals related to atmospheric ^{10}Be fallout processes. ^{10}Be concentrations range from 48.1 to 16.4 x 10^7 atoms/g in the loess-paleosol sequence and from 4.2 to 1.0 x10^7 atoms/g in the fluvial-lacustrine sequence. Two major enhancements in the ^{10}Be concentrations were identified at about 1.4 Ma in section 1 (loess-paleosol) and at about 3.6 Ma in section 2. The mineralogical composition (based on X-ray diffraction) and content of HCl-insoluble material could not account for the enhanced levels of ^{10}Be concentration within the studied sediments. Variation in grain size seems to be an important factor controlling the ^{10}Be concentration in the loess section. This is indicated by a 10-20% higher amount of the <5 µm grains in the Red Loam Formation relative to the younger loess formations. However, the enhancement in section 2 does not correlate with grain size variation between the upper and lower part of the section, because we have chosen equally sorted sediments from all layers of section 2. The most likely explanation of this enhancement is higher ^{10}Be flux before 3.6 Ma as indicated by calculated ^{10}Be flux which shows clustering of the data around two well-defined groups (Fig.2). The first group extends from the top of the modern soil to about 3.6 Ma, and includes the eolian loess, soil, fluvial and lacustrine facies. Here the flux range is 0.7-2.4 x10^6 at/cm^{2}y and the average is 1.8 x10^6 at/cm^{2}y. These are comparable with the estimates for modern atmospheric production and/or flux range. It is interesting that this flux range includes genetically different sediments, which means its validity irrespective of facies. Extending from 3.6-5.4 Ma, the second group comes from the lower part of section 2 and shows an average ^{10}Be flux of 5.1 x 10^6 at/cm^{2}y. This led us to divide the ^{10}Be data within section 2 (fluvial-lacustrine-talus sediments) into two parts for regression treatment. The ^{10}Be concentrations in the studied sediments show linear decay trends over the interval 1.4 to 5.4 Ma (Fig.1). ^{10}Be ages were calculated depending on regression equations. Paleomagnetic chronology has also been carried out for this sediment sequence and correlates generally well with ^{10}Be ages. Climatic information gained from pollen analysis of the fluvial-lacustrine section over the period of 1.8-5.1 Ma shows interesting coincidence with the ^{10}Be flux trend. In both trends a change appears at about 3.6 Ma, where higher ^{10}Be flux is associated with an increase of the subtropic pollen components. Neither the sedimentation rate nor the morphologic and tectonic evolution of the basin support a substantial change of the sediment supply at that time. This may imply a possible change of atmospheric ^{10}Be fallout in the studied region at the turn to Quaternary climate.



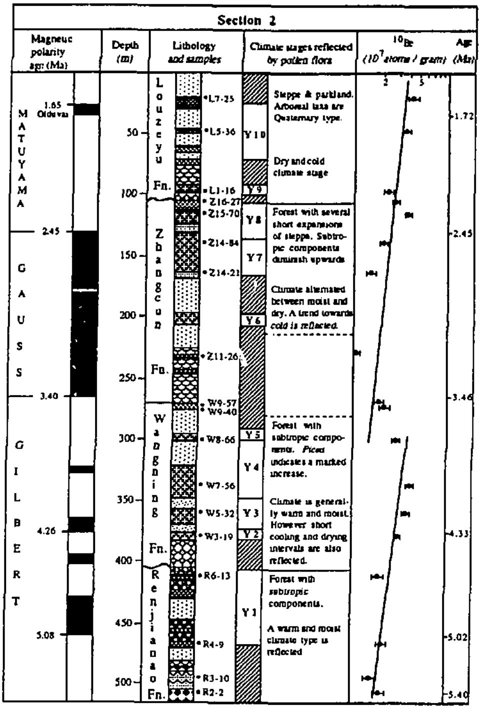


Figure 1: 1, Modern cinnamon loessial soil; 2, Malan Loess; 3, Brown cinnamon paleosol; 4, Lishi Loess; symbols 5-8 for the Red Loam Formation: 5, Brown-red paleosol; 6, Reddish loess; 7, Sandy paleosol; 8, Sandy loess; 9, Unconformity; symbols 10-14 for fluvial sediments: 10, Sand with intercalating clay layers; 11, Calcareous silt and clay; 12, Cross-bedded coarse sand and gravels; 13, Coarse gravel and sand; 14, Gravel and sandy clay; symbols 15-17 for lacustrine sediments: 15, Laminated marl, gyttja and clay; 16, Silt and clay; 17, Fine sand; 18, Coarse talus sediments; 19, Fine talus sediments; 20, Pollen-empty zones.

^{10}Be ages are demarcated by the younger boundary of Olduvai for section 1 and by the boundary of Gauss-Matuyama for section 2. The ^{10}Be value of sample S2-8 was not included for calculation of the regression line.

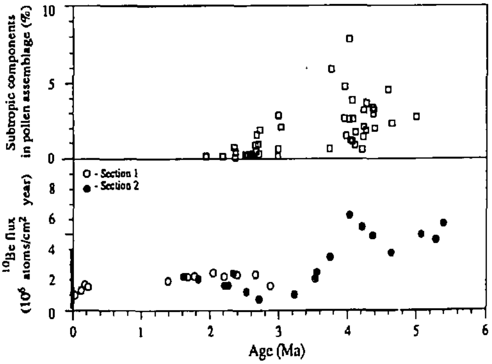


Figure 2: Distribution patterns of ^{10}Be flux and subtropic pollen components versus age. The black bar on the ^{10}Be flux axis indicates range of modern ^{10}Be atmospheric production and flux.

Isotope Composition of Atmospheric Sulphate Near Sour (H_2S-rich) Gas Processing Facilities in Alberta, Canada.

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Emissions from sour gas processing plants in Southern Alberta are composed primarily of sulphur dioxide enriched in ^{34}S relative to sulphur present in the surrounding environment. SO_2 is oxidized to sulphate in the presence of water (acid rain). Sulphate formed in this way is called secondary sulphate as it forms after the emissions leave the stack. Oxygen atoms from atmospheric O_2 and H_2O are incorporated during secondary sulphate formation so that its oxygen isotope composition is a clear indicator of the generation from SO_2.

Data for sulphate in snow collected immediately after three storms near a sour gas processing plant proved particularily interesting. The $\delta^{34}S$ values ranged from +23 down to +11 ‰ for samples which displayed a reverse trend in $\delta^{18}O$, namely an increase from -19 to +2 ‰. The $\delta^{18}O$ values for snow were much more negative, -25 to -30 ‰. Concentrations of sulphate correlated well with both the oxygen and sulphur isotope data. The data leads to the conclusion that the industrial sulphur dioxide emissions from the processing plant had rapidly oxidized during the snowstorms to form sulphate.

Isotope Abundance Measurements of Microgram Quantities of Sulphur

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Conventional Stable Isotope Mass Spectrometry (SIMS), requires 1mg S or more for sulphur isotope abundance measurements. Processing of larger quantities of a sample with trace sulphur is not always feasible. For example, sulphur concentrations in snowmelt from rural regions may be as low as 0.04 mg S per litre so that about 30 litres of snowmelt would have to be subjected to ion exchange techniques. Measurements entail alternately admitting aliquots of sample and standard as SO_2 or SF_6 to the mass spectrometer through capillary leaks under viscous flow conditions. SO_2 in comparison to SF_6 is relatively easy to prepare. However it is readily adsorbed onto surfaces to the extent that with small quantities, the amount adsorbed can constitute a large fraction of the sample.

Successful analysis of trace quantities of sulphur in a large sample (eg. glacier ice, tree rings) is more challenging than for the same amount of sulphur at high concentration in a small sample (eg. a rare hair specimen). In either extreme the ability to analyze μg quantities of sulphur is desirable. Two approaches have been pursued. One, GF-C-CIMS (Gas Flow -Combustion - Current Integration Mass Spectrometry) is an on-line system whereby the SO_2 product is carried by a helium stream through the mass spectrometer source. Ion currents corresponding to masses 64 and 66 are integrated over the time that the SO_2 is in the mass spectrometer. This method has been tested using a Carlo Erba NA1500 interfaced to a Finnigan Delta S mass spectrometer (Giesemann <u>et. al.</u>, 1992). Repeated analyses of two $BaSO_4$ samples realized a precision of ± 0.25 ‰ in $\delta^{34}S$ values for samples greater than 20 μg in size. With smaller amounts, the $\delta^{34}S$ value tended towards that of the standard. Sulphur from 15 spruce needle samples was converted to Ag_2S and analyzed by GF-C-CIMS and conventional SIMS over a range from -3 to +10 ‰. Linear correlation between the two data sets had an r^2 of 0.99 and the average mean difference for a given sample was ±0.2 ‰. Comparisons of Ag_2S and $BaSO_4$ prepared from the same samples by GF-C-CIMS agreed (±0.25 ‰) over a $\delta^{34}S$ range of +4 to +16 ‰ and sample sizes of 10 to 100 μg S.

A similar system using a Prism mass spectrometer is currently being tested. It has the advantage of triple collection of masses 64, 65 and 66 so that comparison of $\delta^{33}S$ and $\delta^{34}S$ values can be used to test for contaminants. However problems with adsorption of SO_2 in the sample preparation/inlet lines have prevented optimal performance.

The second method is solid source mass spectrometry (SSMS). Although analysis with positive ions from AsS_3 is possible (Paulsen and Kelly, 1984), analyses using negative ions from sulphate have been attempted following the work of Wachsmann and Heumann (1992). There has been difficulty in obtaining major SO_2^- currents of greater than 10^{-12} A. Although attempts are being made to increase the rate of ion production, modifications for simultaneous collection and integration of ion currents are being carried out.

At this point, for many sample types (atmospheric particulates, ice cores, soil solutions), conversion to $BaSO_4$ followed by GF-C-CIMS is feasible. Analyses by SSMS is slower, not as convenient, and precision worse by a factor of 5 in comparison to GF-C-CIMS. However SSMS has the possibility of analyses of sub microgram quantities of sulphur. Numerous novel research applications may be pursued with these analytical capabilities.

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MOBILITY OF SULPHUR DURING EARLY DIAGENESIS IN FRESHWATER PEAT: EVIDENCE FROM STABLE SULPHUR ISOTOPES

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Isotopic composition of total sulphur ($\delta^{34}S$) was determined in peat cores from 9 sites in which we previously had characterized changes in the concentrations of organic and inorganic S fractions with depth. The 9 sites, 7 in the United States and 2 in the Czech Republic, have a predominantly Sphagnum-derived peat deposit and were sampled at 2-cm intervals to a depth of approximately 40 cm. Four of the sites in the United States are physiographically minerotrophic, receiving inputs of water both by directly incident precipitation and by runoff from the surrounding upland portions of their catchments. One peat bog, located in the New Jersey Pinelands, is predominantly groudwater fed. Two bogs, one in West Virginia and one in Maryland, have substantially augmented sulphate from inputs of acid coal mine drainage (up to 1200 mg SO_4^{2-} L^{-1}). The peat deposits at the two sites in the Czech Republic are Sphagnum-derived, but there is little living Sphagnum at these sites today, and therefore no current Sphagnum peat accumulation. Whereas Jezerní slat is located in the pristine Šumava Mountains of southern Bohemia, Boží Dar Bog is located in the Krušné hory Mountains of Northern Bohemia, one of the most polluted regions in Europe, affected with massive forest die-back.

At virtually all sites, the isotopic signal to noise ratio was rather high, i.e., the overall range in $\delta^{34}S$ values was substantially greater than differences between $\delta^{34}S$ values for adjacent depth intervals, making it possible to identify shifts in $\delta^{34}S$ that were localized within a series of adjacent depths. All of the sites exhibited a decrease in $\delta^{34}S$ values between the topmost 2-cm section and the sections immediatelly below. Substantial decreases in $\delta^{34}S$ of 6.8 and 11.7 ‰ occured in the top 10-14 cm at the two mine drainage impacted sites. At all sites these near-surface negative isotopic shifts culminated in the minimum $\delta^{34}S$ value obtained in the entire core, in deeper sections of the peat profile $\delta^{34}S$ values increased with increasing depth. Also at all sites the near-surface negative isotopic shifts were accompanied by increases in both organic and, to a much lesser extent, FeS_2-S concentrations, so that in many instances the minimum $\delta^{34}S$ value within a core corresponded to the maximum concentration of organic S and FeS_2-S. More generally, there were significant negative correlations between $\delta^{34}S$ values and concentration of organic S or FeS_2-S in 6 of the 9 cores. The deeper positive isotopic shift was generally accompanied by a decrease in total S concentration.

The near-surface negative $\delta^{34}S$ shift is consistent with the formation of isotopically light C-bonded S by dissimilatory sulphate reduction. The deeper positive $\delta^{34}S$ shift is consistent with the release of isotopically heavy S by mineralization deeper in the peat profiles.

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Redistribution of radium and thorium isotopes as a result of soil formation.

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Natural radioactivity, particularly the various isotopes of radium and thorium, has been identified, in the literature as a useful tool in sediment tracing. In order to uses these tracer nuclides effectively an understanding of their mobilisation and deposition within soil profiles is required. The concentration and distribution of these radionuclides are examined in a valley fill deposit in southern New South Wales, Australia, the lower section of which had undergone soil formation before being overlain by recent alluvial sediments. The site was selected because it enabled the examination of radionuclides in both soil formed from a deposited profile, and in sediment recently deposited at the same location. Well defined correlations between concentrations of ^{226}Ra, ^{230}Th and ^{232}Th exist in the recent sediments, but not in the more altered lower profile. Correlations between radionuclides and major element concentrations are used to demonstrate that both radium and thorium have been deposited in association with Fe/Mn oxides in the soil, mainly at the top of the water table. In growth of ^{210}Pb (the daughter of ^{226}Ra) indicates that this has occurred over a short time period. The variations of major element and radionuclide concentrations down the profile are interpreted in the context of the geomorphic history of the catchment. It is concluded that both radium and thorium isotope concentrations in the valley fill soil are predominantly controlled by secondary processes, rather than being directly inherited from the deposited material. In contrast, the more recent layers appear to preserve the characteristics of the deposited material.

CARBON- AND STRONTIUM-ISOTOPES IN THE RIVER DANUBE AND ITS TRIBUTARIES: TRACERS FOR GEOGENE AND BIOLOGICAL CONTROLS OVER WATER CHEMISTRY

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During 1991 and 1992, the Danube has been repeatedly sampled upstream from Budapest complemented by sampling of 19 major tributaries. Apart from standard chemical parameters, the water samples were analyzed also for C, O and Sr-isotopes.

For the winter campaign, concentrations of dissolved inorganic carbon (DIC) can be interpreted as being entirely derived from carbonate dissolution processes in the catchment area. Due to low temperatures and short daylight, virtually all biological processes such as photosynthesis or bacterial respiration are dormant in the river. Overall, the carbon isotopic composition of DIC and its concentration in the tributaries correlate antithetically, with northern tributaries that drain the Precambrian basement having the lowest DIC and heaviest $^{13}C/^{12}C$. The opposite is the case for southern rivers, draining the carbonate terranes of the Alps, with ^{13}C-values as low as -10 °/oo. Based on these data it can be postulated that the winter DIC in the northern catchments originates from near-surface dissolution of carbonate by acid rain, perhaps stimulated by anthropogenic input. In the southern catchment basins, dominated by carbonates, the dissolution process in the soil zone - catalyzed by bicarbonate derived from oxidation of organic matter - is more effective, yielding the observed higher DIC concentrations. In summer, the $^{13}C/^{12}C$ signal of carbonate dissolution is overprinted by biological processes in the river itself. Extensive photosynthesis adds oxygen to the river water while ^{12}C is removed preferentially from from the DIC-pool. This leads to measurable enrichment in ^{13}C downriver. The Sr-isotopic signal of the Danube is controlled solely by the geology of the catchment area. Radiogenic Sr from the northern tributaries ($^{86}sr/^{86}Sr$: 0.716) mixes in the Danube with less radiogenic one from the alpine rivers ($^{87}Sr/^{86}Sr$: 0.707). Balance considerations show that it is the southern tributaries that control the Sr-isotopic composition of the Danube because of their higher Sr concentrations and water discharge.

Strontium Isotope Characterization of Ground-Water Flow Systems at Yucca Mountain, Nevada, USA

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Yucca Mountain, a broad ridge of Miocene ash-flows in southern Nevada, is being evaluated as a potential site for the construction of a national, high-level, nuclear-waste repository. Among the many site characterization tasks currently being addressed, studies leading to a better understanding of the ground-water flow systems are especially critical in assessing the suitability of Yucca Mountain.

The region is part of the Basin-and-Range physiographic province of the western United States where bedrock ranges alternate with alluvium-filled valleys. Approximately 10,000 m of Late Proterozoic and Paleozoic clastic and carbonate rocks were deposited in this area which was part of the eastern Cordilleran miogeocline. These shelf sequences were severely deformed during Mesozoic compressional tectonics, and subsequently, a thick sequence (ca 1000-3000 m) of silicic ash-flow tuffs was deposited on this structurally complex terrane. Late Cenozoic extensional tectonics deformed the volcanic rocks as well as the underlying Late Proterozoic and Paleozoic rocks.

An exceptionally thick unsaturated zone in parts of the region, including Yucca Mountain, is the result of regional drawdown of the water-table due to the creation of deep sinks such as Death Valley during the Miocene-to-present extension. A change in climate to one of increased aridity, caused largely by uplift of the Sierra Nevada mouintains on the western boundary of the Basin-and-Range province, also contributed to the formation of a thick unsaturated zone. Within the Yucca Mountain area, the saturated zone includes Miocene tuffs, the older shelf carbonate and clastic rocks, and alluvial valley fill derived from the tuffs and the sedimentary units. The Late Proterozoic clastic units, a thick Mississippian-Devonian argillite, and altered parts of the volcanic sequence have been considered in earlier studies to be confining units. The Paleozoic limestones and dolomites, although structurally disrupted, are extensive over eastern Nevada and compose the "regional carbonate aquifer" which is locally confined. Elsewhere the carbonate rocks, the tuffs, or the alluvium are phreatic aquifers. Beneath the potential repository site at Yucca Mountain, the hydraulic head in Paleozoic dolomite is 20 m higher than the head in the overlying Miocene volcanic rocks. Thus, the potential for upward flow exists locally, and conceptually at least, downward flow from the volcanic aquifer into the carbonate aquifer could occur elsewhere.

In addition to conventional water quality and stable isotope data, strontium ($^{87}Sr/^{86}Sr$) and uranium ($^{234}U/^{238}U$) isotope ratios are being measured in ground waters at Yucca Mountain. These radiogenic isotopic systems are proving to be valuable natural tracers and indicators of the degree and extent of water-rock interaction. This paper will deal only with the strontium isotopic data which will be expressed as $\delta^{87}Sr$:

$$\delta^{87}Sr = \{[(^{87}Sr/^{86}Sr)_{gw}/(^{87}Sr/^{86}Sr)_{sw}]-1\}\cdot 1000,$$

where 'gw' is ground water and 'sw' is mean sea water

All of the $\delta^{87}Sr$ values discussed here are relative to a $(^{87}Sr/^{86}Sr)_{sw}$ value of 0.70920.

Within the region of interest, ground-water flow is generally in a southerly direction. Two major flow systems, one in the carbonate sequence and one in the volcanic rocks, seemingly converge south of Yucca Mountain, and which of these or what proportion of each discharge into Death Valley are critical questions.[1] The Ash Meadows system, largely east of Yucca Mountain, is thought to be mainly within Paleozoic carbonate rocks. Major recharge occurs in structurally complex Paleozoic carbonate rocks of the high Spring Mountains (elevation of 3,600 m). High perennial springs have δ^{87}Sr values between -1.1 and 0.8 which are consistent with those of the Paleozoic carbonates through which recharge is occurring (mean δ^{87}Sr of -1.06 ± 0.60). This large flow system discharges along a linear zone at Ash Meadows, south of Yucca Mountain, where most of the springs show a limited variability in δ^{87}Sr (mean value of 4.65 ± 0.19); these values are substantially larger than those at recharge in the high Spring Mountains. Had the ground water encountered only Paleozoic carbonate rocks along the flow path from, the δ^{87}Sr of the springs would not have increased over the values at recharge. Three springs at the southeastern end of the Ash Meadows discharge zone show strongly elevated δ^{87}Sr values between 11.0 and 13.9. These ratios and extremely large δ^{87}Sr values of 33.5 to 38.8 for perennial springs emerging from Late Proterozoic clastic rocks upgradient in the northwestern Spring Mountains suggest substantially more flow through and interaction with the Late Proterozoic section than conceptualized in earlier hydrologic models.

The water table at Yucca Mountain is within silicic ash-flow tuffs at a depth of approximately 750 m at the potential repository site. Recharge is thought to occur at higher elevations to the north at Pahute Mesa where limited δ^{87}Sr data range from 0.3 to 3.0. δ^{87}Sr values increase progressively southward with a local variation of about 3‰ in δ^{87}Sr. Saline waters at Franklin Lake playa, a discharge site at the southern end of the system, show less variability with δ^{87}Sr values clustering between 5.0 and 6.3. Higher δ^{87}Sr values, up to 10.7, occur in ground water at the southwestern end of the system along the northeastern side of the Funeral Mountains (Amargosa Desert) where Late Proterozoic clastic rocks crop out. In Death Valley along the southwestern side of the Funeral Mountains, large springs emanating largely from Paleozoic limestones carry δ^{87}Sr as large as 13.8. These large δ^{87}Sr values on opposing sides of the Funeral Mountains suggest that lateral flow into the Paleozoic rocks occurs from the upgradient volcanic and alluvial aquifer of Yucca Mountain and the Amargosa Desert.

Continued radiogenic isotopic studies in concert with other hydrochemical and hydrologic studies in the Yucca Mountain site characterization project will address (1) possible leakage between the two major aquifers, (2) the extent and location of ground-water flow through Late Proterozoic rocks, (3) the source of ground water discharging into Death Valley, and (4) the identification of ground water sources for paleospring deposits now well above the water table.

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AMS radiocarbon applications in environmental and climatic sciences.

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Carbon is the most essential element of life and thus of central importance when studying dynamic processes in our environment. The existence of the natural radioisotope ^{14}C ($T_{1/2}$= 5730 a) offers a unique possibility to trace mobility and transportation in-between different reservoirs. The limiting factor in most of the radiocarbon applications since the introduction of the method in the 1950th has been the amount of material required for an analysis, namely >1 g carbon in the conventional decay counting technique. The introduction of the ultra sensitive accelerator mass spectrometry (AMS) technique has circumvented this restriction. Presently only >100μg carbon is enough for an analysis. The Uppsala tandem accelerator system has been improved in order to meet the special demands of the AMS method and chemical pretreatment procedures have been developed to handle organic (cellulose, amino acids etc.) as well as inorganic (carbonate, atmospheric and aquatic carbon dioxide etc.) carbon samples in the milligram range.

The technique has until now been applied to explore several environmental and climatic related problems. Recent processes have been investigated through exploring the so called "atomic bomb" effect around 1960 which has caused a doubling of the atmospheric activity within a couple of years. As examples three different ongoing projects utilizing this spike are presented. The present climatic warming is, too a large extent, anticipated the "Green-house" gases especially the CO_2. To model and predict future climate change, it is of central interest to understand the carbon exchange between the atmosphere and the oceans. We have undertaken depth profiling of Atlantic ocean water (fig.1) from different stations sampled by the Swedish polar icebreaker expedition ODEN-91 according to the ^{14}C activity making estimate of the boundary conditions in the circulation and exchange possible. The "bomb activity" has been traced by studying chronological sequences of oak tree rings (fig.2). This is relevant since the cellulose in each cell is formed in equilibrium with the atmosphere. Furthermore, release of methane and carbon dioxide from peat bogs has been investigated with respect to the "Green house" gases. A comparison between moss increment and radiocarbon shows about 20% of the carbon dioxide to be released from older and deeper parts of the bog to the atmosphere.

Finally we also like to present an interesting project that has become feasible because of the small amount of sample required in AMS, namely dating of rock fissures and ground water by solved or precipitated calcite and/or humics. A series of sites in connection with possible nuclear waste deposition have been studied.

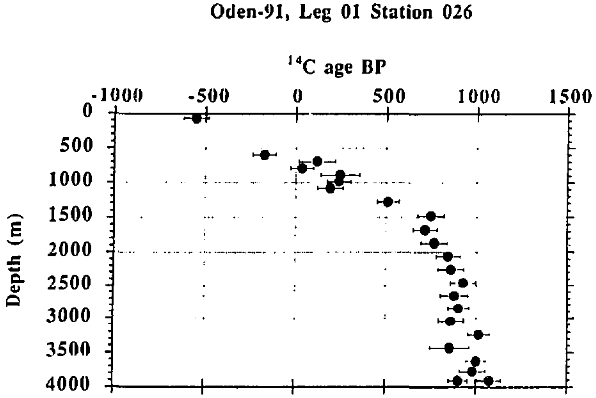

Figure 1. Radiocarbon activity at different depths in a sea water profile close to the north pole sampled by the Swedish icebreaker ODEN.

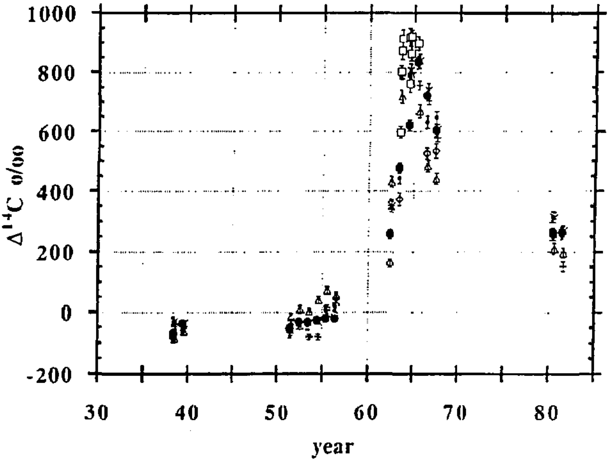

Figure 2. Radiocarbon activity in different chemical fractions of tree rings from an oak grown in the suburb of Uppsala.

Sulphate Isotope Signatures in New Zealand Rivers

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The work presented here forms part of a joint study on sulphate in rivers of England and New Zealand, investigating pristine and polluted sites, to determine the differences in sulphate concentration and sulphur and oxygen isotopic compositions with respect to geological and anthropogenic inputs. Preliminary data on four New Zealand rivers and their main tributaries are reported here. These are, in the North Island: the Whangaehu river system, flowing from the eastern slopes of Mt Ruapehu, an active andesitic volcano, through Tertiary and Quaternary sediments to the west coast; the Hutt and Wairarapa valley rivers, flowing through Mesozoic greywacke, Tertiary/Quaternary sediments, and through areas of intensive agriculture. In the South Island, the Buller and the Wairau flow over more diverse geology to the west and east coasts respectively. Sulphur isotope data are presented in per mille deviation from CDT and oxygen isotope data relative to VSMOW.

The Whangaehu river usually receives overflow from Mt Ruapehu Crater Lake. Injection of fumarolic steam and gases into the lake cause the river to be highly mineralised and of low pH. In Dec 1992, the sulphate concentration was 1580 mg/kg in the headwaters, decreasing to 71 mg/mg near the coast. Tributaries not affected by volcanic activity have about 10 mg/kg sulphate. The Hutt and Wairarapa valley rivers range generally from 2 to 4 mg/kg sulphate and 4 to 12 mg/kg chloride. However, two samples showed increased concentrations of up to 16 mg/kg sulphate and 28 mg/kg chloride. The South Island rivers have lower values, ranging from 1 to 5 mg/kg sulphate and around 2 mg/kg chloride.

River water δ^{18}O values vary from around -6.2‰ (Hutt and Wairarapa) to -8.5‰ (Whangaehu) and -8.9‰ (Wairau). However, in the Ruapehu Crater Lake the δ^{18}O values of the water increase up to about +2‰ due to evaporation. Also the very low pH and higher temperatures promote rapid exchange of oxygen isotopes with the sulphate and of sulphur isotopes with reduced sulphur species. Thus the Crater Lake sulphate has δ^{34}S values up to +18‰ and δ^{18}O values up to +20‰. As the river flows down the volcano and into Tertiary/Quaternary sediments, the δ^{34}S values decrease from +17 to +13‰ and δ^{18}O values from +12 to +10.5‰. Tributaries flowing in from the sediments have negative δ^{34}S values and δ^{18}O values around +5‰, thus inducing the trend of decreasing values shown in Fig. 1.

Mixing also appears to be present in the Hutt and Wairarapa river systems. Lower δ^{34}S and δ^{18}O values (around +5‰ and 1 to 2‰ respectively) typify sulphate derived from the greywacke rocks. Tertiary sediments again influence inputs with negative δ^{34}S values. The Hutt river system appears to lie between a greywacke end member and sea water sulphate (see Fig. 1). All the samples are from within 30 km of the coast and there may be an overprint of sea water sulphate spray. Chloride/sulphate weight ratios are about 4, compared to sea water at about 7. In the Wairarapa, these ratios range from 7 at the coast to less than 1 inland. The Hutt and Wairarapa samples mentioned previously with the higher sulphate and chloride concentrations also have higher δ^{34}S values (up to +16‰) and δ^{18}O values (up to +9‰), but the chloride/ sulphate ratios are as low as 2; i.e. not consistent with sea water. They are from intensively farmed areas in Quaternary sediments. Widely used in these areas, superphosphate fertiliser (produced from sulphuric acid and phosphate rock, with isotope values shown in Fig. 1) appears to have contaminated the rivers. The samples do not project exactly to the fertiliser composition which may have preserved into the river system its sulphur but not its oxygen isotopic composition.

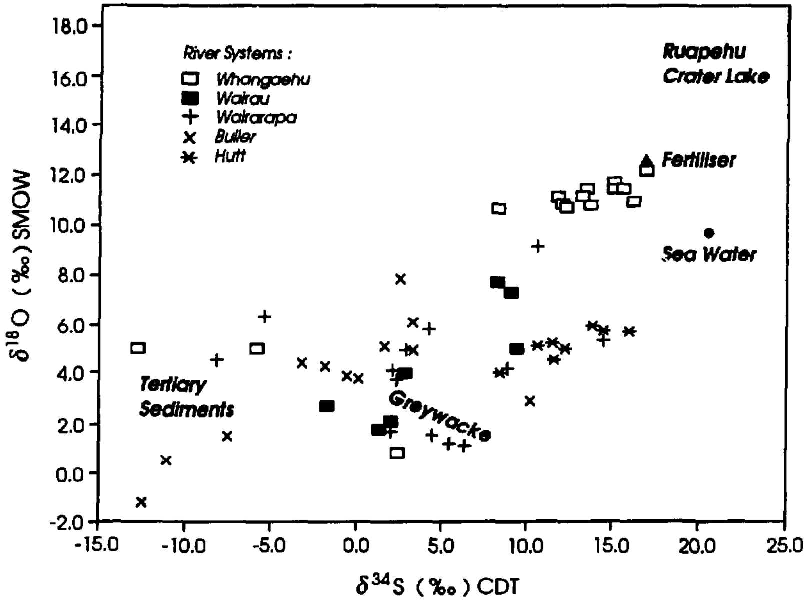

Fig. 1: Isotopic compositions of some New Zealand river water sulphates and sulphate sources.

The Wairau river system sulphates vary from +9 to -1‰ in sulphur isotopic compositions and from +7 to +2‰ in oxygen isotopic compositions. Tributaries with the highest δ-values drain schists, ultramafics and older sediments to the north. The tributaries draining in from the south flow through Mesozoic greywacke producing the lower δ-values, similar to the North Island localities. Tha Buller river and tributaries range from +10 to -12‰ in sulphate sulphur isotope values and from +8 to -1‰ in oxygen isotope values. This river system drains a more diverse geologic terrain: the main discernible feature is negative sulphur isotope values from the rivers in Tertiary sediments, similar to North Island localities, but with lower δ^{18}O values (see Fig. 1). The South Island rivers show a gross trend of decreasing isotope values as sulphate increases from about 2 to 6 mg/kg. Presumably, pyrite oxidation in Tertiary sediments imparts an increase in sulphate concentration, negative δ^{34}S values and incorporation of more water oxygen in the oxidation process to explain the lower δ^{18}O values.

The data derived thus far demonstrate that river water sulphate from different geological inputs can usually be differentiated by sulphur isotope signatures, and to a lesser extent by oxygen isotope signatures. A combination of isotopic ratios and chemistry is needed to discriminate fertiliser sulphate in New Zealand from sea water sulphate. More work is required to understand sulphate production pathways and mechanisms which impart different oxygen isotopic compositions.

MAPPING OF RESERVOIR HYDRODYNAMIC SYSTEMS
"an application of the natural $^{87}Sr/^{86}Sr$ isotopic tracer"

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The method makes it possible to examine the anatomy of hydrocarbon reservoirs through analysis of natural variations of $^{87}Sr/^{86}Sr$ in precipitated salts extracted from dry cores, with special emphasis on characterization of barriers and high permeability zones.

A central theme in reservoir geology is gaining information about the degree and pattern of pore volume communication within the reservoir. One approach is to examine the chemistry of the pore fluids, i.e. the hydrocarbons or formation waters since fluids in communication should have uniform chemical composition in contrast to isolated ones.

A new technique has (since 1986) been developed at Institutt for energiteknikk (IFE) in which we perform indirect measurements of the $^{87}Sr/^{86}Sr$ ratio in the pore water by analyzing pore salts dissolved from disaggregated chips of dry core. Evaporation-redissolution processes and changes in concentration of Sr do not affect the $^{87}Sr/^{86}Sr$ ratio of the pore salts which mirrors the original pore water composition. Tailor made tests show that mud filtrate contamination is not a problem, provided the samples are taken from the central part of the cores.

Diagenetic reactions occurring in a reservoir, particularly where this involves dissolution of minerals with widely differing $^{87}Sr/^{86}Sr$ ratios (e.g. carbonates, feldspars, micas) will develop local heterogeneities of $^{87}Sr/^{86}Sr$ in the water. Such heterogeneities would tend to be subsequently dispersed by diffusive (or other) mixing processes unless there are permeability barriers preventing this. Every reservoir, or reservoir zone may thus be unique concerning its $^{87}Sr/^{86}Sr$ ratio. That is, if it's not in connection with other reservoirs or reservoir zones.

Barriers can be of different kind, like shales, carbonates, sealed faults, asphaltene layers, etc. and thus restrict the reservoir vertically and horizontally. In a plot of Sr-ratios of formation water (residual salts) versus depth, possible barriers may be identified (see figure).

The $^{87}Sr/^{86}Sr$ ratio can also be used to identify the effect of high permeability zones acting as plumbing systems in which water (e.g. compaction water) have preferentially migrated into the reservoir from one or more distant sources.

Where variations in formation water $^{87}Sr/^{86}Sr$ correlate with sample mineralogy, this information will also be of value for determining the nature of recent diagenetic reactions and their influence on pore water chemistry. When such information is combined with other data on authigenic minerals, the timing of barrier formation may be determined, together with the diagenetic evolution of the reservoir.

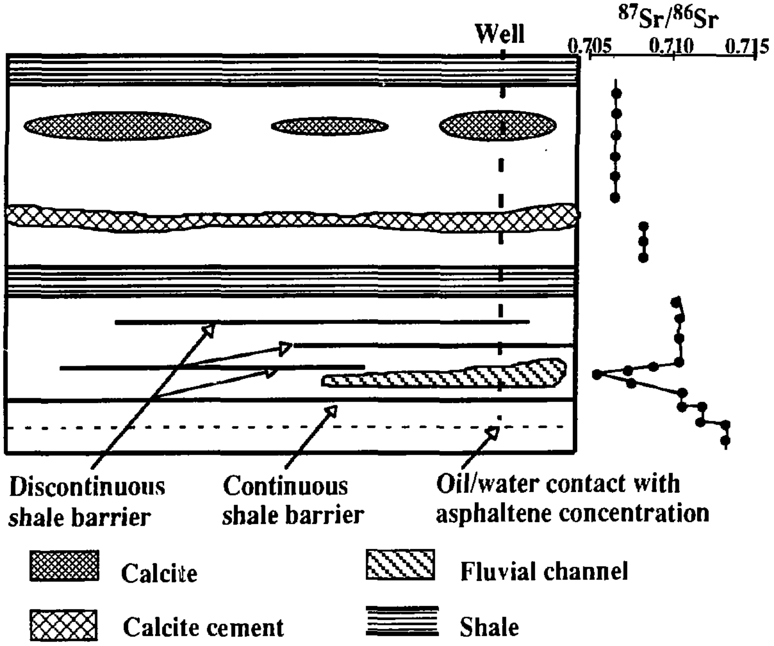
The data we have obtained on reservoirs, using the techniques described above, are extremely interesting and encouraging and the method is already being extensively applied. Even though the method in theory should work best in sandstone reservoirs, because of the more deversified mineralogy, the method also appears to work well in carbonate reservoirs *.

Based on our experience, sampling (on the average) every second meter would be appropriate in order not to miss any anomalies which often is a result of thief zones within the different reservoir units. With todays analytical accuracy it is possible to measure even small scale variations within individual reservoir units.

A project should be done in cooperation with production geologists and reservoir engineers working on the field of interest. This cooperation is regarded as extremely important to ensure the integration of data such as; pressure test data, sedimentological considerations, data on porosity and permeability, and thus be able to make the best possible interpretation.

**Smalley P.C., Lønøy A., and Råheim A., 1992: Spatial $^{87}Sr/^{86}Sr$ variations in formation water and calcite from the Ekofisk chalk oil field: implications for reservoir connectivity and fluid composition. Applied Geochemistry Vol.7, 341-350.*

$^{87}Sr/^{86}Sr$ profile through sandstone reservoi



STABLE ISOTOPE GEOCHEMISTRY APPLIED TO PALEOCLIMATOLOGICAL AND GREENHOUSE GAS PROBLEMS

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The stable isotope ratios of hydrogen and oxygen in ice cores from glaciers and polar ice sheets have been used as an empiric surface "paleothermometer", and for age dating through the use of "annual isotope variations". It will be pointed out that in several cases short term variations of H and O isotopes in ice cores cannot be interpreted as "annual cycles", and that such variations are obliterated in old ice. This is due to a number of physico-chemical processes including melting, sublimation, freezing, and condensation operating in situ and in the ice cores leading to redistribution of H and O stable isotopes when the sample cannot be considered a closed system (see Jaworowski, Segalstad & Ono 1992: Do glaciers tell a true atmospheric CO_2 story? *Science of the Total Environment* 114, 227-284).

An assumption of a closed system with respect to H and O isotopes does not hold for the firn strata. The release of vapor by sublimation of the ice in an open system will leave the remaining ice enriched in D and ^{18}O isotopes. Artifacts from H_2O state changes due to thermal gradients, both natural and during core drilling, may be falsely interpreted as changes in the paleotemperature of snow precipitation. H and O stable isotope data from glacier and polar ice cannot be regarded as a reliable basis for estimation of past climate changes. Core samples reportedly stored for 16 years before isotope analysis, which had lost 30% of their mass through sublimation, will, if also the condensed vapor is considered, have changed the H and O stable isotope ratios of the remaining ice vs. the condensed vapor to a level corresponding to the whole "paleotemperature" range in the Vostok (Antarctica) core. H and O isotope fractionation processes, starting immediately after precipitation of snow and occurring until analysis of ice cores, will *change the stable isotope composition in ice. The isotopic changes may be of the same magnitude* even larger, than the range reported from deep ice cores. Such changes contain no quantitative information on surface paleotemperatures or paleoclimates, but are rather due to a combination of paleotemperature variations and later physico-chemical processes.

Carbon isotopes in CO_2 gas in ice have been shown to be negatively correlated with the CO_2 concentration, ascribed to the release of carbon into the atmosphere from man's burning of fossil fuel. Such a negative correlation will, however, be expected through a combination of solubility and isotope fractionation as a function of the temperature gradient in ice sheets. The oxygen isotopes of CO_2 in gas inclusions in ice show that there has been equilibration between the gas and the bubble wall. Hence the assertion, that the CO_2 variations found from analyses of ice cores reflect exclusively an atmospheric change, mainly due to man's burning of fossil fuels, does not hold.

Stable $^{13}C/^{12}C$ isotope ratios (expressed as $\delta^{13}C_{PDB}$) can be used to compute the composition of atmospheric CO_2. The natural atmospheric CO_2 reservoir has $\delta^{13}C \approx -7$‰ when in isotopic equilibrium with marine HCO_3^- and $CaCO_3$. CO_2 from burning of fossil-fuel and biogenic materials has $\delta^{13}C \approx -26$‰.

$\delta^{13}C$ reported for atmospheric CO_2 was -7.489‰ in Dec. 1978, decreasing to -7.807‰ in Dec. 1988 (Keeling et al. 1989; *AGU Geophys. Mono.* 55, 165-236). In ~300 years old Antarctic ice $\delta^{13}C = -6.31$ of trapped CO_2 (Friedli et al. 1986; *Nature* 324, 237-238).

If the decreasing $\delta^{13}C$ was only caused by mixing natural CO_2 with CO_2 from burning of fossil fuels or plants (current ~79%/~21% CO_2 mix; lifetime 50-200 years; *IPCC* 1989), the current atmospheric CO_2 $\delta^{13}C$ should be much lower than reported.

The December 1988 atmospheric CO_2 composition was computed for its 748 GT C (GT = 10^{15} g) total mass and $\delta^{13}C = -7.807$‰ for 3 components: *(1)* natural fraction remaining from the pre-industrial atmosphere; *(2)* cumulative fraction remaining from all annual fossil-fuel CO_2 emissions; *(3)* carbon isotope mass-balanced natural fraction. The masses of component *(1)* and *(2)* were computed for different atmospheric lifetimes of CO_2.

The result fits a lifetime of ~5 (5.4) years, in agreement with ^{14}C studies. The mass of all past fossil-fuel and biogenic emissions remaining in the current atmosphere was ~30 GT C or less, i.e. maximum ~4%, corresponding to an atmospheric concentration of ~14 ppmv.

The implication of the ~5 year lifetime is that ~135 GT C (~18%) of the atmospheric CO_2 is exchanged each year. The isotopic mass balance calculations show that at least 96% of the current atmospheric CO_2 is isotopically indistinguishable from non-fossil-fuel sources, i.e. natural marine and juvenile sources. Hence for the atmospheric CO_2 budget marine equilibration and degassing and juvenile degassing from e.g. volcanic sources must be much more important, and burning of fossil-fuel and biogenic materials much less important, than hitherto assumed.

Acknowledgements: Technological Oriented Studies, University of Oslo, for financial support; Dr. Zbigniew Jaworowski for scientific discussions and contributions.

INCREASE OF RESOLUTION IN U/Pb DATING USING REFINED MINERAL SEPARATION TECHNIQUES.

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Modern petrological, geochemical, metallogenic and tectonic exploration not only requires precise isotope data to distinguish geological processes and the formation time of the rock units and minerals but also the age of their protoliths and of later metamorphic overprints. Because a variety of effects can disturb the isotope systems, only the most resistant accessory mineral, zircon, can be successfully and simultaneously used for high-precision U/Pb age determinations of all the above mentioned geological phenomena. On the other hand, the resistant nature of zircon leads to the presence in the rock of the several distinct zircon generations and thus will provide meaningless, average age information in case the total zircon population is analyzed. Only in the last two decades several morphological features of zircon crystals were recognized as genetic indicators and as a consequence isotopic dating was increasingly performed on handpicked fractions of grains of the same origin. Advances in microanalytical techniques now permit analysis of single-grain zircons selected on the basis of their genetic peculiarities.

However, the majority of the published single-zircon studies reveal that the individual zircon grains may display a complicated composition. Due to intermittent growth and recrystallization from origin to present time, these single grains normally consist of phases that differ in age and which possibly correlate with discrete petrological events of the host rock's history. For a geologically meaningful interpretation we must be sure that the analyzed single-zircons represent a particular geologic event. In our study of the Hercynian granitoids from the Gotthard massif, central Swiss Alps, we attempted both to minimize secondary alteration effects and to locate the truly monophase zircon grains which define the geological events.

Our approach is based on the following petrological premise:

1) Granitoid intrusions may contain four principal classes of accessory zircon: a) an inherited population which survived the process of protolith(s) mobilization; b) a population incorporated from wall rocks during xenoliths assimilation; c) a magmatic population crystallized from melt; d) a metamorphic population which grew during secondary events or which represents totally recrystallized earlier crystals.

2) Approximately 90% of the bulk accessory zircons are located in interstices (along intergranular boundaries) which are most permeable for circulating secondary fluids.

3) Petrographically established crystallization sequences of the rock-forming minerals indicate the presence of early and late magmatic as well as secondary metasomatic feldspar, quartz and micas.

4) While magmatic and metamorphic zircon can be generated over a range of conditions, certain rock-forming minerals grow under more limited PT-conditions and their relative ages can clearly be determined.

5) Zircons included in these minerals may thus have formed at different stages of the rock's history and moreover the zircons may have been protected against later metamorphic fluids.

6) After mobilization or partial melting of protolithic material, newly crystallizing rock-forming minerals may be able to entrain and enclose ancient zircon grains.

7) The best "mineral cans" for preserving the zircons are the feldspars, which in turn may consist of several generations from early magmatic plagioclase through late magmatic orthoclase to metasomatic microcline. Shielded from reactions taking place outside the feldspar, the chance for later overgrowth or recrystallisation of such zircons is clearly reduced.

To make use of this insight, our zircon separation technique involves at least the following steps:

- Jaw-crushing of rock specimens to observed size of feldspar grains or sawing feldspar megacrysts in case of porphyric texture of the granites
- Ultrasonic cleaning of hand-picked feldspar grains
- Separation of feldspar grains into different mineralogical phases on the basis of their optical properties
- Hand-crushing of the feldspars to expected size of the included zircon grains
- Additional cleaning of resulting powders by magnetic separator
- Extended centrifuge separation of the accessory minerals in methylene iodide or Clerici solution
- Final hand-picking of zircons most clearly exhibiting the peculiarities associated with their suspected genesis.

In comparison with U/Pb isotope data of conventionally separated single zircons, the zircons extracted from feldspars demonstrate that:

1) The majority of zircons from feldspars are devoid of overgrowing rims and/or old cores, they contain much fewer solid inclusions and are practically free of cracks

2) Magmatic zircons extracted from orthoclase and plagioclase of Hercynian rocks are not affected by later Alpine greenschist to amphibolite facies metamorphism which particularly affected the Hercynian magmatic zircons separated from whole rocks

3) The inherited zircons are preserved as whole grains in the early magmatic plagioclase where they keep the Precambrian radiogenic Pb composition. The extremely rare zircons of similar morphology from intergranular matter are almost completely recrystallized during the Hercynian magmatic event

4) ^{206}Pb/^{238}U ages for zircons separated from metasomatic microcline porphyroblasts coincide with the published Rb/Sr whole-rock age and thus indicate the post-intrusive recrystallization nature of this event.

Isotope studies within the hydrogeochemical site investigations by Teollisuuden Voima Oy, Finland

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1. Introduction

In 1987 Teollisuuden Voima Oy (TVO) started preliminary field investigations at five sites, in order to determine the suitability of Finnish crystalline bedrock for the final deposition of spent nuclear fuel. The sites were Romuvaara (shortened RO, gneiss), Veitsivaara (VE, migmatite), Kivetty (KI, migmatite, Syyry (SY, tonalite) and Olkiluoto (OL, tonalite). Generally one deep borehole (1 000 m) and four shorter ones (500 m) were drilled at each site. This paper evaluates the isotopic data (H-2, O-18, H-3 and Rn-222) gained during 1987-1992 from these preliminary investigations. Some C-14, C-13, U(tot) and U-234/U-238 data was also gathered, but they are more thoroughly discussed in the hydrogeochemical summary report of TVO (Lampén and Snellman, 1993).

2. Description of the actual work

The main goals for the hydrogeochemical site investigations were to characterize and classify the water samples, evaluate the representativeness of the data, and to produce input data for geochemical modelling and the performance assessment.

Local background reference data was gained by sampling bored domestic wells and natural springs, brooks and lakes from a larger area around the actual site. Monthly precipitation during at least one year was collected at each site, too. At the site, besides the deeper investigation boreholes, also shallower boreholes (100 m) aiming at flushing water production or hydrological studies were sampled. The TVO groundwater sampling equipment (Rouhiainen et al., 1992) using either single- or double-packer techniques was used in pumping the deeper boreholes. The flushing water during the drilling activities was labelled with uranine and iodide. These and some field parameters were monitored at the surface constantly during the sampling campaign lasting typically for about 7-10 days from one level. In 1991 TVO developed a multi-packer system to prevent mixing of different groundwaters through open-hole effect. These boreholes were also sampled.

The water samples were analyzed with an extensive programme. Main variables and constituents, trace elements, stable and radioactive isotopes and evacuated gases were analyzed of nearly all groundwater samples. The environmental reference samples were studied especially for the stable isotopes, H-2 and O-18, and tritium.

3. Results

The most prominent difference of the general hydrogeochemical features of the sites was the salinity of the groundwaters. At Romuvaara, Veitsivaara and Kivetty, the groundwaters are fresh, and at Syyry and Olkiluoto, the groundwaters are fresh, brackish or saline.

The proportion of the stable isotopes H-2 and O-18 in the water samples from all five sites refer to a meteoric origin, and on the average, the values are located clearly below the GMWL.

There may be some erroneous trends due to the long sampling period of the precipitation samples (30±2 days). On account of isotopic fractionation, the precipitation during the warmer season are clearly heavier than those collected during winter. The lightest water samples were obtained from the most northeastern areas, Romuvaara and Veitsivaara, and the heavier ones from the most southwestern area, Olkiluoto. Samples of surficial waters and precipitation seem to refer to local meteoric water lines.

The observed tritium values for the groundwater samples varied between 3 - 55 TU. There was no clear trend between tritium and the amount of remaining flushing water, or amount of pumped water. On the other hand, there is a clear decreasing correlation between tritium and sampling depth or concentration of chloride.

The highest amounts of Rn-222 were observed in the groundwaters at those sites where the bedrock contains minerals rich in uranium and thorium. Especially at Veitsivaara the radon values were approximately 5 000 Bq/l.

4. *Discussion*

Some stable isotope values from groundwaters in the deep boreholes at Romuvaara, Kivetty, Syyry and Olkiluoto areas refer to colder infiltration conditions. Especially at Olkiluoto, on the western coast of the Gulf of Bothnia, large differences were observed between the boreholes and the different sampling depths. The observed δH-2 and δO-18 values for local shallow groundwaters can be explained by a mixing of old, glacial water with present-day seawater (Blomqvist et al., 1992). The chemistry and abscence of depletion of δH-2 and δO-18, as compared the shallower groundwaters, suggest that the saline groundwaters are not derived from the geochemical evolution of overlaying waters, but rather from a partly separate, deeper aquifer (Pitkänen et al., 1992).

On the average, the lower tritium values were observed at sites with brackish and saline groundwaters, i.e. Syyry and Olkiluoto. This agrees well with the concept that longer mean residence times of groundwaters with water-rock interaction processes of longer duration produce increased salinity.

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Nitrogen Isotope Determination on Minute Gas Quantities

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BGR is investigating nitrogen isotopes from natural gases in Northern Germany and from pyrolysis experiments of potential source rocks within the frame of a Deep-Gas-Project. Nitrogen concentrations range from 0.1 to 85 vol%. Two different laboratory systems are used:

- A conventional preparation line for the separation of nitrogen from a natural gas (EGA-Erdgas-Aufbereitung) and following isotope analysis in a conventional isotope ratio mass spectrometer (IRMS; MAT 250).
- A gas chromatograph is directly connected with the isotope ratio mass spectrometer (GCIRMS).

The advantages of the GCIRMS system mainly are i) analysis of gas with low nitrogen concentration (< 0.1 %), ii) prevention of sample contamination by atmospheric nitrogen, which occasionally yielded errors up to 2 ‰ in $\delta^{15}N$ values using the EGA line and iii) user-friendly and fast operation.

The GCIRMS-system is equipped with a column (ca. 2m, 1/4 ") packed with 5 Å molecular sieve held at a temperature of 75 °C. The head pressure of the He carrier is about 280 kPa. Through a multi-sampler, a cold trap and a multiport valve the sample is introduced into the gc. The MAT 250 isotope ratio mass spectrometer (no differential pumping) is connected with the gc by an interface, mainly consisting of two variable vacuum-splits. The ion signals of the masses 28/29/30 are simultaneously monitored by the three collectors of the MAT 250. Data is acquired by a PC using an IEEE-interface for standard communication. MS signals are detected with an integration time of 0.1 sec. A special software was developed for data processing and PC-controlled peak integration.

During operation, the cold trap (liquid nitrogen temperature) of the inlet system retains condensable components like heavier hydrocarbons, carbon dioxide and water. It helps to increase peak separation between nitrogen and methane and to increase the nitrogen output to the ms. By the variable vacuum splits in the transfer line from the gc to the ms the column-pressure is reduced to the ms-pressure and the split ratio can be adjusted to the nitrogen concentration of the sample. Oxygen and argon are online monitored to detect a possible air contamination of the samples and to calculate the air-free $\delta^{15}N$.

To achieve accurate isotope data, the absolute δ-scale is fixed by international standards (NGS-1, NGS-2, air) which are used to calibrate the different internal laboratory standards (-7 ‰ $< \delta^{15}N <$ 14 ‰). Each sample data is controlled by measurements of these standard. The GCIRMS-system allows the $\delta^{15}N$ determination on gases with nitrogen in the concentration range of ca. 0.1 - 100 Vol% which corresponds to 0.2 to 200 µl of nitrogen. The accuracy of the measurements is 0.2 ‰ - 0.5 ‰ and depends on the sample size.

Nitrogen isotope data from more than 200 natural gases from Northern Germany were analysed. Some results will be briefly discussed: A comparison with published data show significant deviations (up to 30‰). $\delta^{15}N$ values from pyrolyses experiments of the Upper Carboniferous coal seams are used to model generation processes of the natural gases.

Analysis of $\delta^{18}O$ in silicates using a laser microprobe system with benzene (C_6H_6) vapour as reducing agent

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Oxygen for $\delta^{18}O$ determination is normally extracted from silicates by heating the sample in the presence of a halogen fluoride gas such as BrF_5 or ClF_3. The oxygen extraction is performed in a special line. The sample can be heated with a suitable laser system or a tailor-made oven.

It is, however, difficult to obtain high quality halogen fluoride gases. Moreover, these gases are highly toxic and their utilisation in a laboratory demands rigorous safety measures. It is, therefore, of interest to find other less hazardous reducing agents, which can be used in the extraction of oxygen from silicate material.

At Institutt for energiteknikk we have used different reducing agents in a laser probe system, such as carbon coating of the sample, and different hydrocarbon gases in the reaction chamber. The application of carbon coating is impractical because the amount of carbon is too small and it is also difficult to observe the sample. The tests were also negative for methane (CH_4) and ethane (C_6H_6). Benzene (C_6H_6) gave a spontaneous reaction.

The silicate sample is exposed to a laser beam from the Nd-YAG laser (7W) in a chamber with a benzene atmosphere. The oxygen from the silicate is converted to CO and H_2O (with a trace of CO_2). Benzene and H_2O are removed from the gas mixture with the help of a pentane- based trap. The CO is adsorbed on silica gel at the temperature of liquid nitrogen and transported to a high voltage chamber, where the CO is transformed to CO_2. This transformation requires that the reaction is complete (i.e. all CO molecules are transformed to CO_2). To obtain a complete reaction of CO to CO_2 the high voltage treatment is continued for 5 minutes after the first reaction is "finished" by addition of a small amount of super pure He to the chamber. The CO_2 formed during the transformation is continuously frozen into a suitable sample holder.

The results of our experiments are very encouraging. 11 tests on a quartz standard gave a total range in the $\delta^{18}O$ between 10.21 ‰ and 11.93 ‰ , with an average of 11.1. Results on the same standard by conventional bulk methods from two laboratories gave $\delta^{18}O$ values of 11.2 ‰ and 11.0 ‰, respectively. The good agreement between these results suggest that there is no isotopic fractionation when oxygen is extracted from silicate material by the use of benzene vapour in the reaction chamber.

The range in the $\delta^{18}O$ values, using the benzene method, is most likely due to the difficulty in obtaining a complete transformation of CO to CO_2. A better method would be to measure the $\delta^{18}O$ value directly on the CO gas. We believe that this can be achieved by linking the laser system directly to the new generation of gas chromatograph gas mass spectrometers.

Areas after open cast lignite mining including waste deposits - an isotope hydrological case study from Kanena/Halle, Germany

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Lignite mining was the main source of energy in Eastern Germany and resulted in numerous extended open pits. This is accompanied by diverse disturbations in the ecology, water cycles and geochemical conditions. Coal fragments and sulphides from the new, mixed and aerated overburden influence the quality of the new ground- and surface water depending on variable conditions during the mining and filling processes. Furthermore, abandoned excavations from mining were often used to deposit numerous urban and industrial wastes in a more or less uncontrolled and undocumented manner.

Thus, large devastated and often polluted areas have to be recultivated after finishing the lignite open pit mining. New lakes are generated by rising groundwater or flooding with surface waters. Complex efforts are necessary to minimize the spreading of dangerous or unwanted substances and to create a stable system suitable for normal landuse or natural refuge.

An example of a closed subaqueous waste deposit within an open lignite pit is the former mining area Kanena/Halle. The abandoned and partially recultivated area contains a waste deposit site of about 0.25 km^2 located over redistributed sediments and surrounded by the horseshoe shaped lake "Hufeisensee" with a surface of about 0.75 km^2. From the end of the thirties up to 1984 wastes such as ashes from power plants, urban garbage, chemical and probably military residues were deposited more or less continously.

In 1990 first projects were started to study the chemical state and the flow regime in the deposit-groundwater-lake system and to evaluate the risk for further pollutant migration as well as to show possibilities for prevention. Recently isotope studies (deuterium, oxygen 18 and tritium) were integrated into a complex hydrogeological and chemical-biological investigation programme to characterize different water bodies as to their origin, mean residence time of the water and exchange processes.

Specially we were able to document that

1. Remarkable evaporation effects exist in the well mixed upper zones of the lake. This was also observed to some degree within the waste deposit which we explain with water trapped from a former existing pond. This shows the existence of more stagnant water bodies within the deposit.

2. In contrast to that the deepest zone of the lake "Hufeisensee" and the greater part of the deposit are characterized by the isotope signature of the surrounding groundwater. The deepest lake water is higher mineralized than the overlying lake water and controlled by reducing conditions. Significant exchange does not exist at the boundary surface between both water bodies.

3. The origin of the mineralized waters in the deepest lake zone can not be explained mainly by recent inflow from the deposit into the lake. Ascending Zechstein water or leaching water from the early time of depositing must be the source.

4. No evidence of significant tritium input by nuclear wastes was found similar to other studied deposits from this region.

The Grenvillian-Alpine evolution of Pb-Zn mineralization in Spitsbergen: Pb-isotope evidence for the post-Tertiary rejuvenation.

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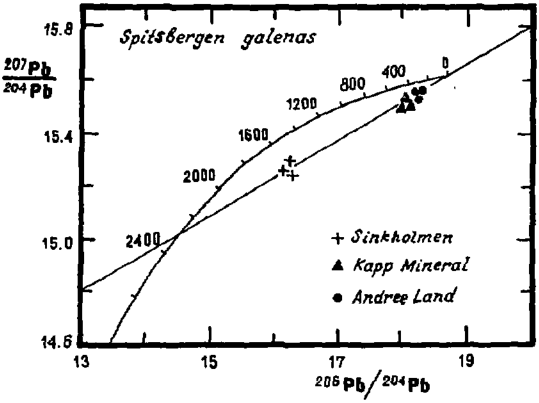
The Spitsbergen archipelago represents the most northwestern block of the Eurasian continental plate within the Barents Shelf, where different geotectonic units such as young cratonic cover and old mobile belts are in a close contact with the North Atlantic Ocean tectonic structures. The Carboniferous-Paleogenic cratonic cover is framed by the Tertiary thrust-fold belts and transcurrent fault systems (Harland and Horsfield, 1974; Bergh and Andersen, 1990; Haremo et al.,1990). The Tertiary tectonic movements caused reactivation of major lineaments in the archipelago.

Pb-Zn mineralizations predominantly occur within the Late Proterozoic succession that composes Vestspitsbergen Orogenic Belt. The mineralizations are mostly represented by hydrothermal veins which occure within the definite stratigraphic levels of the succession. Geololgical data suggest the pre-Vendian origin of carbonate-shale metasediments (Turchenko, 1987; Bjornerud, 1990), hosting the Pb-Zn mineralization. Recent U-Pb, Sr and Nd isotope data point to the Grenvillian tectonothermal activity within the region (Peucat et al.,1989) and also to the exisistence of the Early Proterozoic crystalline basement (Gee et al.,1992).

The Devonian molasse rocks underlie the young cratonic cover and host Pb-Zn vein mineralizations as well. The mineralizations occure along the eastern border of the Grokammen ridge (Andree Land) and coincide with the Billefjorden Fault Zone. Here, submeridional fault system was filled with the galena-bearing quartz veins.

Galena Pb-isotope compositions of the known Pb-Zn occurrences Sinkholmen and Kapp Mineral, located within the Late Proterozoic succession as well as of the vein mineralization within the Devonian rocks (Andree Land), were measured. In the Pb-Pb coordinate system the data for 9 studied samples plot below the Stacey-Kramers growth curve and form a linear array (Fig). The regression line intersects the growh curve in two points corresponding to the model ages of about zero and 2300 Ma. This kind of ore lead isotope distribution is typical for so called "rejuvenated cratons" (Zartman, 1984). The data point to an old crustal source of the ore lead and to the Alpine or even younger tectonic and hydrothermal rejuvenation of Svalbard platform along the Tertiary thrust-fold and fault zones.



FINE FRACTIONS OF ARGILLITES FOR THE Rb-Sr DATING: SEPARATION, XRD AND TEM STUDIES

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Fine clay fractions were separated from four samples of Upper Vendian shales of the East European Platform and studied by the X-ray powder diffraction (XRD), transmission electron microscope (TEM) and Rb-Sr methods. Two samples were collected from the Medvedevo-1 borehole, the Nizhni Novgorod region (depth ca. -1850 m, the Ust-Pinega Formation, the Middle Redkino horizon). Two other samples were collected from the Gavrilov Yam-2 borehole, Yaroslavl region (depth ca. -2540 m, the Ust-Pinega Formation, the Lower Redkino horizon).

The samples were crushed and standard separation of <2 μm fractions were made by sedimentation in distilled water. From these <2 μm fractions six subfractions (<0.1 μm, 0.1-0.2 μm, 0.2-0.3 μm, 0.3-0.4 μm, 0.4-0.6 μm and 0.6-2.0 μm) were separated by centrifugation. The size distribution of clay particles in each subfraction was monitored by TEM technique.

Morphology and mineralogy of the clay particles in coarser and finer subfractions are markedly dissimilar. The 0.6-2 μm fraction involves the platy xenomorphic crystals. The <0.1 μm fraction is constitued by the lath-shaped crystals with irregular partly ragged ends. Both morphological species occur in the intermediate fractions. Higher magnification for the 0.4-0.6 μm and 0.3-0.4 μm fractions revealed that laths or fibers grew on the cores of xenomorphic grains. As the size of the particles decreases, a mixed-layer illite/smectite arises, the content of smectite layers being at its maximum of 15-20 per cent in the <0.1 μm fraction. The illite crystallinity index (the width in $\Delta 2\theta$ of the

10A diffraction peak at half height obtained by an analysis of an oriented sample) increases gradually from the values of 0.35-0.40 for the 0.6-2 μm fractions to 1.48-1.60 for the <0.1 μm fractions. The content of chlorite decreases in the finer fractions.

The Rb-Sr model dates for the 0.6-2 μm and <0.1 μm fractions differ by the value of about 200 Ma. The dates for the 0.6-2 μm fraction are significantly older than those acceptable for the Upper Vendian, hence the xenomorphic illite inherent in this fraction is detrital. On the conttrary, the dates for the <0.1 μm fraction are slightly younger than "stratigraphical" age and imply an autigenic origin for the lath-shaped species of illite. The <2 μm clay fraction is thus composed of at least two illite generations differing in morphology, crystallochemestry and the Rb-Sr age.

Fractions with the size of particles less than 2 μm are of current use in geochronological studying and estimating metamorphic transformation of argillaceous rocks. This paper shows that both an apparent isotopic age and an illite crystallinity index for such fractions may be nor more than the weighted means for uncogenetic constituents of the rock. To obtain a real geochronologic and petrogenetic information the <2 μm fraction should be separated into several subfractions involving particles which are as uniform in size as possible.

Using stable isotope data to define the causes of carbonate trapping

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No abstract

δD, $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$, and $\delta^{87}Sr$ Systematics in Ground Water and Hydrogenic Deposits at Äspö, Sweden

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Ground water and calcite fracture fillings at the Äspö (the site of the SKB's Äspö Hard Rock Laboratory) show wide ranges in stable and strontium isotopic compositions. None of the isotope signatures resemble those of modern Baltic sea water although the possibility of mixing between Baltic sea water and shallow ground waters cannot be excluded. δD values ranges between -112 to -55 o/oo and $\delta^{18}O$ values range between -7 and -15 o/oo. The $\delta^{13}C$ of the bicarbonate range between -16 and -6 ‰, and decrease systematically with depth suggesting mixing of organic and inorganic carbon. The $\delta^{18}O$ is uniform (+18 and +22 ‰) and in equilibrium with the most of the ground water. $\delta^{34}S$ values of the dissolved sulphate varies between +9.8 to +21 o/oo. $\delta^{87}Sr$ values (per mil deviation of $^{87}Sr/^{86}Sr$ from modern sea water) of ground water define two populations.

Eighteen samples from 15 to 800 m deep have $\delta^{87}Sr$ values between +10. and +13.9 in contrast with five samples of Baltic Sea water collected in the vicinity of Äspö with $\delta^{87}Sr$ values between +0.2 and +0.4 - only slightly larger than open ocean water. In contrast, two ground water samples from approximately 100 and 300 m have much lower $\delta^{87}Sr$ values of -2.2 and -2.5. The 1.8-Ga host rock at Äspö is characterized by low Rb/Sr ratios, and a calculated mean $\delta^{87}Sr$ of approximately +2.5 illustrates the lack of isotopic equilibrium between the ground water and the host granite at the bulk rock scale. However, preferential dissolution of high Rb/Sr phases such as biotite cannot presently be discounted. Alternatively, the large $\delta^{87}Sr$ values reflect recharge and flow through much more readiogenic rocks prior to reaching Äspö. Calcite fracture fillings add further complexity to the Sr-isotope budget. Six calcite fillings from depth between 363 and 612 m have $\delta^{87}Sr$ values between +4.7 and +9.9 whereas one deep sample (815 m) has much lower value of -3.0 coupled with an order of magnitude higher Sr concentrations.

$\delta^{13}C$ values in the calcite fissure fillings range between -48 and -3 ‰ and the $\delta^{18}O$ values range between +15 to +26 ‰.The large range in $\delta^{13}C$ values is indicative of multiple sources for the carbon, including atmospheric, organic and methane derived carbon. The $\delta^{18}O$ signatures suggest mixing of meteoric and marine waters, but some of the calcites could be in equilibrium with the modern ground water.

The stable isotope data from the calcite fissure fillings and the dissolved species suggest three different water layer at Äspö: (1) a shallow ground water (0-150 m) characterized by a mixture of meteoric water and minor proportions of Baltic Sea water, (2) an intermediate ground water (150 - 500 m) characterized by a mixture of marine and meteoric isotope signatures, and (3) a deep ground water body (>500m) which is highly saline with nonmarine signatures of the dissolved species. According to the seasonal variation of the isotopic signature (δD and $\delta^{18}O$) of the rain water the recharge of this water lens takes place during the autumn and the winter. The intermediate water body, characterized by a considerable drop in the $\delta^{34}S$ values of the dissolved sulphate indicate an inmixing of a nonmarine component. This suggest a contribution of reduced sulphur from the fracture sulphides. Therefore the sulphur and oxygen isotope data combined for that water suggest that it originates from an early injection of a highly oxygenated Baltic seawater after the latest ice recession in the area. The deep ground water body reveal a stable isotope assembly with overall typically nonmarine signatures. However, the spread in $\delta^{34}S$ values of the dissolved sulphate in combination with the sulphide sulphur signatures suggest that considerable bacterial sulphate reduction takes place in the upper part of this water body.

Boron Concentration and Isotope Abundance Measurements. Comparison of Negative Thermal Ionization Mass Spectrometry and Inductively Coupled Plasma Techniques.

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Traditional gas source stable isotope mass spectrometry requires sample sizes of the order of milligrams of the element of interest. Although this technique is preferred for good precision, suitable boron-containing gases are difficult to prepare and analyze mass spectrometrically. Further, since the abundance of boron in nature is low, it is sometimes difficult to extract sufficient amounts for analyses. Positive ion solid source mass spectrometry has the advantage of precise analyses with sub-microgram quantities of material and is routinely used (Bassett, 1990). However, this method suffers from somewhat complicated preparation techniques, lower ion current, and isobaric interferences if $Na_2BO_2^+$ ions are measured. More recently, negative thermal ionization mass spectrometry (NTIMS) is emerging as a tool which readily permits reliable isotope abundance measurements with nanogram size samples (Zeininger and Heumann, 1983).

Investigations with an in-house built NTIMS at the Stable Isotope Laboratory at the University of Calgary have focused on environmental waters. Precise isotope and concentration measurements with minute samples can provide desirable information on sources, natural cycling, and transport of boron and related pollutants. Boron isotope compositions were measured using BO_2^- and concentrations determined by isotope dilution techniques. Waters with more than a few ppm boron require no pre-treatment and are deposited directly on a Re filament for NTIMS analysis. Low boron content solutions are passed through ion exchange resins for concentrating. The concentration data were compared with those obtained by inductively coupled plasma analysis performed at the Institute of Sedimentary and Petroleum Geology.

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CARBON ISOTOPIC COMPOSITION OF VHEVELLITE ($CaC_2O_4 . H_2O$) FROM DIFFERENT GEOLOGICAL ENVIRONMENTS AND ITS SIGNIFICANCE

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Abstract

Vhewellite ($CaC_2O_4.H_2O$) is a rare mineral occurring in the cracks of carbonate concretions (septarian nodules) in argillaceous rocks of sedimentary basins rich in organic matter, especially in those containing coal seams. Vhewellites from lower temperature hydrothermal veins were previously also described. Vhewellite of this type was found in uranium and Bi-Co-Ni hydrothermal veins, quartz - calcite - fluorite veins and in quartz veins associated with organics and sulfides.

Carbon isotopic composition of whewellite ($CaC_2O_4 . H_2O$) varies significantly among individual types of occurrences from the Bohemian Massif, Czechoslovakia. The $\delta^{13}C$ values of whewellite found inside pelosiderite concretions in the coal-bearing Kladno Carboniferous basin are unusually high from + 3.2 to + 14.7 $^{o}/_{oo}$. In the Tertiary Northern Bohemian Basin, where the depth of burial and coalification grades are much lower, the $\delta^{13}C$ values of two whewellite samples are -6.9 and -14.2 $^{o}/_{oo}$. Vhewellites from low-temperature hydrothermal veins of the Příbram uranium deposits, where bacterial processes are highly unlikely, have $\delta^{13}C$ values of

-31.7 to -28.4 $^{o}/_{oo}$, identical to carbon isotopic composition of underlying black shales.

Based on our data it is probable that whewellite from carbonate concretions in argillaceous rock sequences rich in organic matter, especially in those with deeper burial, have systematically high $\delta^{13}C$ values. Intramolecular or intermolecular carbon isotopic fractionation is in all likelihood not large enough to produce such large shifts to higher $\delta^{13}C$ values. Bacterial fermentation processes resulting in isotopically heavy residual oxalate seem to have been involved. Whewellite from the hydrothermal uranium-bearing veins has light carbon isotopic composition in the range of normal $\delta^{13}C$ values of organic matter. Oxalate formation seems to be related to the hydrothermal oxidation of organic matter.

ABSTRACT

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REPRODUCIBILITY OF THE ISOTOPE-GC TECHNIQUE

Examples and data taken from organic geochemical samples

Introduction

In recent years there have been a number of publications on stable isotope analysis of single hydrocarbons in oils and extracts. New instrument developments have made it possible to undertake rapid, direct stable carbon isotope analysis. However, few publications excist that discuss the analytical technique in itself and its implications on the reproducibility of the data.

This paper discusses some aspects of the technique as experienced at Geolab Nor through our work with stable isotope analysis of organic geochemical samples. It is believed that the same problems/considerations in general will apply to the analysis of other types of samples as well. In particular the paper will discuss the effect on reproducibility while performing the "heart cutting" process as opposed to allowing the whole run through the mass spectrometer, the use of background subtraction packages, the intensity of the individual compounds and its impact on the reliability of the analytical results, the coelution of compounds, and isotopic fractionation as an effect of storage and evaporation.

All the work described here is undertaken on a VG Isochrom II instrument, and all the work is performed at Geolab Nor.

Results and discussions

No significant difference was observed between the "heartcutting process", called IRMS, and the GC-IRMS where the whole sample is allowed to run through the mass spectrometer. The analysis show good reproducibility, and mean $\delta^{13}C$ values which show less than 0.3% variation between the two techniques.

In order to analyze the effectiveness of baseline subtraction procedures, the isotopic composition of n-alkane fractions were determined, with and without baseline subtraction procedures. For samples with a significant background, baseline subtraction is essential to produce reliable data. For samples with little or no background, background subtraction is of less importance.

The reliability of the analytical results are closely linked to the amount of the compound analyzed, i.e. the peakhight (intensity) of the individual compound. The isotopic values deviate strongly from the average when the peaks are minor. If the major beam is less than E-8 Amp, the data are unreliable. Peaks with values less then E-8 Amp should therefore not be quoted.

Overlapping will lead to inaccurate results. On low maturity samples, coelution of steranes and triterpanes with n-alkanes in the high molecular weight range is observed. This problem can be solved by separating the saturated fraction in two - one of n-alkanes and one of branched/cyclics -by use of silica lite. Coelution of the compounds are avoided, and both n-alkanes and steranes/triterpanes can be analyzed. A more difficult problem to solve is overlapping steranes that can not be separated. The isotopevalue observed is a mean of isotope values from two peaks with different isotope composition. With maturity, the ratio of the overlapping compounds change - and thus also the isotopevalue observed. It is therefore important to recognize the limitations of the results whenever overlapping peaks are present. On reporting steranes, peaks that represent two compounds or more should always be indicated as a composite peak.

There has been sceptisicm about the usefulness of isotopic composition of data from oils, due to the likelihood of isotopic fractionation during storage, so the results depend largely upon the length of storage of the samples. Two tests were performed; an evaporation test and a test of natural fractionation. The conclusions of these experiments is that C_5 - C_{20} can be used with confidence for oil/condensate correlation even though storage methods and times can vary considerably. No indication of natural isotopic fractionation between the analyzed condensates and the oils were observed.

The $^{87}Sr/^{86}Sr$ ratio as an environmental tracer

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Natural isotopic systems like strontium have proved to be good tracers for the monitoring of processes of the past and the present. Especially when combining different parameters like minerals, soil, water and biological material for the study of environmental changes over shorter as well as longer time periods. Depending on environmental conditions, material and backround the strontium $^{87}Sr/^{86}Sr$ ratios have unique values for different environments. A few examples are given.

Two lakes were sampled monthly during one year in order to study seasonal variations in the isotope ratios. The ratios varied in a narrow range except during the spring thaw period when the ratio of the surface water was lowered by a contribution from melting snow. Large masses of snow with a strontium ratio of ca. 0.710 had accumulated during winter. At the clearing of ice the snow ratio had a sudden impact on the surface water which was lowered from 0.732 to 0.728 but it was soon evened out due to low Sr concentration in the snow in comparison to that of the lake water.

For runoff water there is a reverse relationship with discharge. High Sr-ratios are associated with low discharge. Abundant rainwater with a low Sr-ratio will have a greater impact on the runoff value at high discharge. The residence time for the soilwater will also decrease with increased precipitation and thus limit the time for interaction with the soil minerals.

Contrasting rock compositions in river basins, especially when combined with large age differences, results in greatly differing isotope ratios for river waters. In Sweden and Finland rivers with a discharge rate over 150 m^3/s have $^{87}Sr/^{86}Sr$ isotope ratios between 0.728 and 0.735, while streams with discharge rates between 1-50 m^3/s have their ratios spread out over the interval 0.718 to 0.736. The cause being the occurrence of rocks with low isotope ratios. In a small drainage area they may be important but for a larger drainage area this situation is unlikely.

A study of major elements, stable isotopes and Sr ratios in a snow profile across the Caledonides, from west to east, showed rapidly decreasing concentrations of the elements, an increase in Sr ratios and decreasing oxygen and hydrogen ratios with distance from the Atlantic Ocean. The easternmost sample gives low ratios for O and H and low concentrations for Na and Cl, which is to be expected. The $^{87}Sr/^{86}Sr$ ratio and the S concentration, however, reaches their highest values along the transect. This sample is obviously strongly influenced by anthropogenic pollution, probably from the wood pulp industry localized here.

$^{87}Sr/^{86}Sr$ results from Central Sweden yielded ratios around 0.71 for precipitation. Throughfall (below the canopy), with ratios of the order of 0.72-0.73, is a mixture of atmospherically transported Sr caught by vegetation and Sr from the mineral soil. Further results showed that shallow ground water in a dug well and runoff water had ratios of around 0.73-0.74 and water from a fracture zone in a stream gave a value of 0.78. The rock in the fracture zone had a strontium value of 0.85 to 0.90.

Analyses of the ^{87}Sr/^{86}Sr ratio for soil samples shows weathering to be related to the size of the mineral grains. Smaller grains have a lower Sr ratio compared with larger grains. The explanation may be that the smaller grains greater surface to volume ratio results in a stronger weathering ability which in turn may give rise to a preferential leaching.

In depth profiles the total soil samples show high Sr ratios in the uppermost layer which then decrease strongly by depth to a certain level where the values stabilize. The higher ratios are due to more K-rich minerals in the uppermost part of the soil which is depleted in more easily weathered Ca-rich ones which is also seen from the Ca and Sr concentrations. Soil water samples follow the same depth trend as the soil samples but have lower strontium ratios which is natural. The decrease in strontium ratios appear here in the first 5 to 10 cm. However, within an area, some 100 m^2, at the same depth, the soil is quite homogeneous having similar strontium ratios.

The uppermost soil-layer, -3 to 0 cm depth, consisting of humus (organic matter), is enriched in products that have passed up through the trees and then been deposited in the form of needles and twigs on the ground. Leaching of this soil layer with NH$_4$Ac gives a value similar to that of the throughfall. Leaching of the next layer, the upper mineral soil (0-15 cm), yields a slightly higher strontium value than that recorded for the soilwater and also a higher value than that of the previous humus layer. But the trend is the same as for the first 20 cm as for the soil samples.

Analyses of Swedish fresh water mussel shells from 1915 to 1990 show a distinct decrease in ^{87}Sr/^{86}Sr ratio over time, from ca. 0.7334 down to ca. 0.7325. One locality was treated with lime in the 1980:s. The effect was clearly registered in the ^{87}Sr/^{86}Sr ratios for the mussel shells.

This decreasing trend is same found when analyzing the calcium content and the ^{87}Sr/^{86}Sr ratio of bark and tree rings in the vincinity of the fresh mussel locality. A study of bark of spruce, pine and birch from two areas the bark from spruce and pine gave similar values while the birch ratios were slightly biased towards higher values. This deviation might be due to the different root system of the birch. In the third area, spruce and pine trees gave similar ratios for bark and the trunks outermost growth-layer. The results showed an obvious decrease both in element uptake and ^{87}Sr/^{86}Sr ratio by the spruce tree. That is, the Sr content had decreased from ca.15 ppm 1942 to ca.5 ppm 1985 and the ^{87}Sr/^{86}Sr ratio from 0.7278 to 0.7163.

Isotopic analyses of an oak tree growing along a main road in the outskirts of Stockholm showed a decrease in ^{87}Sr/^{86}Sr ratio from 0.7351 to 0.7240 between 1810 and 1990. A similar study of a pine from outside Oslo showed same decrease in Sr ratios between 1860 and 1950, 0.7216 to 0.7207, but then an increase up to 1980 of 0.7213.

The spread and variation in the ^{87}Sr/^{86}Sr ratios thus makes Sr isotopes a powerful tool when it comes to monitoring changes in the environment. Sampling of the past is a difficult task but is made possible by using biological material, in combination with inorganic material. Isotopic systems make it possible to study any area in any place over a certain time interval. There also exists the possibility of using museum collections where trends in environmental changes can be studied.

Laser determination of weathering depth and provenance by carbon and oxygen isotopes

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Abstract

Laser probe microsampling of C and O from carbonate minerals for isotopic analysis was achieved by focussing a Nd:YAG high-power laser through microscope optics onto a sample situated in a vacuum chamber. The laser beam, about 10 µm in diameter, was used to ablate an area on the sample, liberating CO_2 gas. The CO_2 was purified and led directly into a mass spectrometer for isotopic analysis. Preliminary tests of 9 samples of the lime-cemented Gotland sandstone from different surroundings in Sweden show that the laser microprobe is an excellent tool for estimating depth of weathering, condition and earlier treatment of lime-cemented stone objects. Analysis were made on drill-cores, from the surface of the object and inwards. All samples analyzed gave similar trends with depth for the carbon and oxygen isotopes. However, this trend was modified depending on exposure, location, biologic overgrowth, salt efflorescence, earlier conservation etc. A great advantage with the laser technique is that the operator can change area of analyses and that no material is lost due to preparation and cutting as in conventional work.

In order to replace stones at a restauration, get proper material for laboratory tests before conservation etc., a knowledge of the way it changes in colour and structure due to weathering is of utmost importance as the original quarry of building-stone is usually not known. Carbon and oxygen analyses of rock samples from different quarries and stratigraphic levels show that it is possible to fingerprint the provenance areas. In the present study, seven bulk samples from five quarries were analyzed for carbon and oxygen isotopes. The $\delta^{13}C$ values of samples at the same stratigraphic level show a distinct geographical pattern, with decreasing values from north to south. One quarry also shows decreasing values when going downwards in the stratigraphic sequence. This means that it might be possible to unveil the provenance of lime-cemented building stones of unknown origin by using carbon isotopes.

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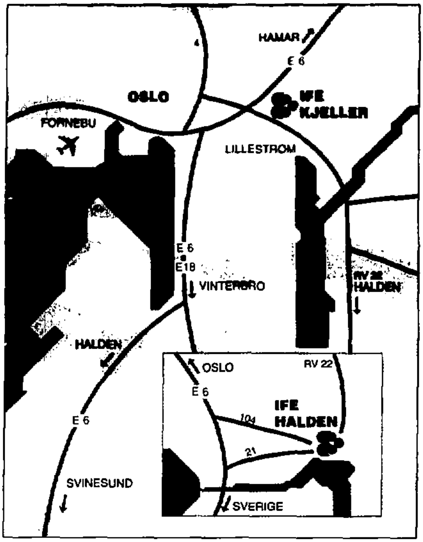

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