European Society for Isotope Research

Isotope Workshop Volume

ESIR

7th Workshop

Seggauberg, June 27 - July 1 2004

Hosted by:

Karl-Franzens University
Department of Earth Sciences
Geology and Paleontology
&
Landesmuseum Joanneum
Department of Mineralogy

Bojar, A.-V., Fritz, H., Bojar, H.-P., (Eds.): 7th Workshop of the European Society for Isotope Research.- Ber. Inst. Erdwissenschaften, Karl-Franzens Universität Graz, Band 8, 172 S., Graz, 2004.

Herausgeber und Verleger: Institut für Erdwissenschaften, Bereich Geologie und Paläontologie, Karl-Franzens-Universität Graz, Heinrichstrasse 26,
A-8010 Graz, Österreich

Redaktion, Satz und Layout:
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Druckerei:
Offsetdruckerei der Karl-Franzens-Universität Graz, Cover: Xerox Steiermark

Berichte des Institutes für Erdwissenschaften, Geologie und Paläontologie der Karl-Franzens-Universität Graz
<ISSN 1608-8166>

Stable isotope study in a paleosol horizon of the Quaternary Vár-hegy travertine (Budapest, Hungary)

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Beside the classic geological (sedimentological) and geomorphological studies, the investigation of travertines in Hungary recently turned to the geochemical analysis of sediment material and determination of possible links between geochemistry and lithofacies. Geochemical data, mostly stable C and O isotope compositions of Quarternary travertines occurring at several places in Hungary were recently published by Kele et al. (2003) and Földvári et al. (2003).

Quarternary travertine occurrences sometimes contain paleosol horizons which are result of former subaerial exposure periods. The study of paleosol horizons is very important in reconstructing past environmental conditions.

We studied the paleosol horizon intercalated into the travertine of the Vár-hegy (Castle Hill) in Budapest. One of the methods applied was stable isotope analysis of carbonate phases of the paleosol. Results were compared to the stable isotope composition of travertine, because comparison of data may indicate the amount of carbonate of pedogenic origin in the paleosol, thus providing information about the stage of development of pedogenesis.

The Quaternary sequence of the Vár-hegy starts with basal clastic strata, which are overlain by travertine. The lower part of the travertine is laminated, muddy and rich in terrestrial and freshwater fossils and plants. The top of the laminated travertine is a subaerial unconformity surface, on which a paleosol layer of 15 to 50 cm thickness was developed. The paleosol horizon has a great lateral extension (200 to 400 m) and is covered by a 7 to 8 m thick massive travertine poor in fossils and plants. The basal layer of paleosol is made of calcareous muddy sediments covering the karstic surface of travertine. The main level of paleosol consists of two horizons macroscopically; the lower one is richer in carbonate:

grains are penetrated and surrounded by white, thin and loose calcareous coatings and fibers at some places.

Microscopic observations on the paleosol and calcareous cavity fills revealed that they are mostly made up of mechanically reworked travertine clasts with a variable amount of allothigenic siliciclastic (e.g. quartz, mica and rock) fragments. Traces of carbonate reprecipitations can also be detected in thin sections: needle-fiber calcite in vugs and pores and micritic carbonate precipitations (hypocoatings) around pores of the paleosol and cavity fills. These secondary carbonate precipitations can result from biogenic processes during pedogenesis, therefore may indicate the possible influence of vegetation during their accumulation.

Bulk carbonate samples of paleosol and cavity fills (which do not contain secondary carbonate visible to the naked eye), paleosol samples rich in secondary carbonate and pure secondary carbonate precipitations were analysed for stable isotope composition. The oxygen isotope composition of the Vár-hegy travertine is between -17.7 and -13.7‰ (relative to V-PDB), while its carbon isotope composition has a narrow range from 1.1 to 2.1‰ (Földvári et al., 2003). Pure secondary (pedogenic) carbonate precipitations have significantly different isotope compositions (average: $\delta^{13}C$ = -7.3‰, $\delta^{18}O$ = -7.1‰) compared to that of the travertine (Fig. 1). Paleosol samples rich in secondary carbonate have intermediate isotope compositions between travertine and secondary precipitations, which indicate that they are mixtures of these two endmembers (Fig. 1).

Isotope composition of bulk paleosol and cavity fill samples partly overlaps with that of the travertine, but half of the samples have slightly lower $\delta^{13}C$ values (Fig. 1). Results indicate that bulk paleosol and cavity fill samples contain no or only minor amount of pedogenic carbonate. The amount of pedogenic carbonate can be estimated from the carbon isotope composition of the two endmembers (Nordt et al., 1998). Calculations show that bulk paleosol contains up to 16%, whereas bulk cavity fill contains up to 25% pedogenic carbonate.

Stable isotope results indicate that formation of authigenic carbonate is subordinate in the bulk paleosol material, which points to a weak *in situ* pedogenesis. Carbon isotope composition of pure secondary carbonate suggests that during pedogenesis the flora was mostly composed of C_3-type plants.

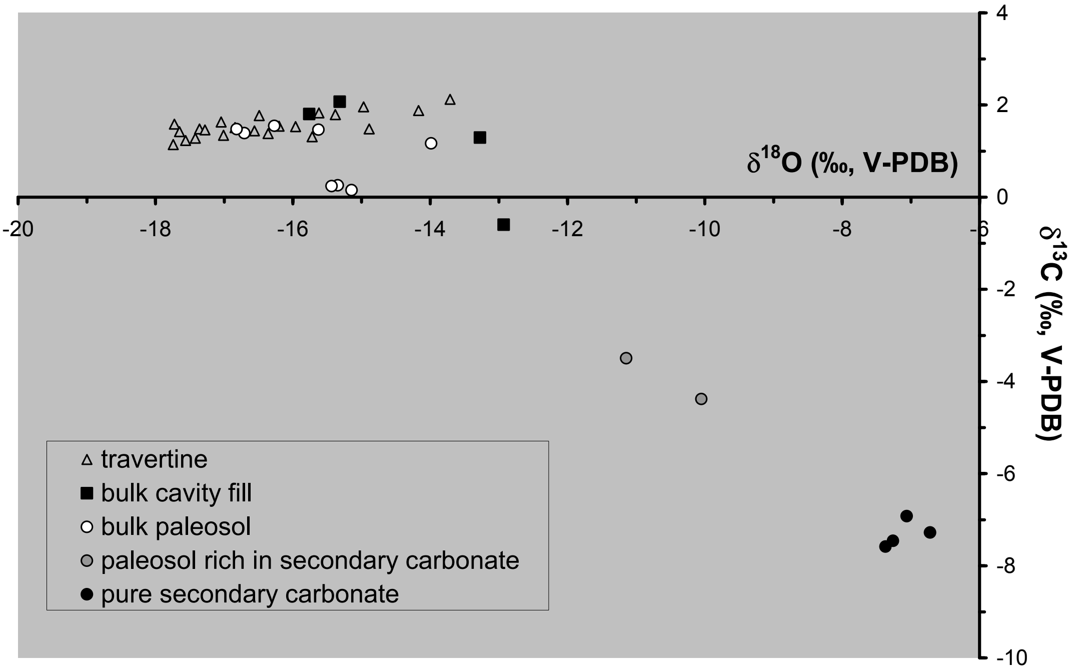

Fig. 1. Oxygen vs. carbon isotope composition (in ‰ relative to V-PDB) of bulk paleosol and cavity fill samples, paleosol samples rich in secondary carbonate and pure secondary (pedogenic) carbonate precipitations from the paleosol horizon of the Vár-hegy travertine. The isotope composition of the Vár-hegy travertine is mostly from Földvári et al. (2003).

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Isotopic investigation on the origin of the mineral waters from Someşeni, România

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The isotopic study (^{18}O, D) of mineral waters from Someşeni Spa is important in the tentative to reabilitate them as natural curative waters. The studied area, Someşeni Spa, is located in the eastern part of Cluj-Napoca, Romania. From a geological point of view, the mineral aquifer is located on the western border of the Neogene Transylvanian Basin. The therapeutical qualities of this waters were known since the early 1920's and the spa was established in 1927. The first scientific studies on the mineral waters from Someşeni were completed in the early 1920's with some researches on their chemical composition and medical properties.The detailed physical and chemical analyses were performed by the Institute of Balneology and Physioterapy (Institute of Balneology and Physioterapy, 1965).

From the hydrologycal point of view, our researches by deuterium analyses have presumed that these waters are related to a unique aquifer, and the differences in the physical and chemical properties of the sources are related to the different ways in which these waters are followed in the vicinity of the salt body (Baciu et al., 2001).
The water samples were collected monthly for five investigated springs: No. 1, No. 2, No. 3, No. 8, No. 15 , and also for Becaş Brook and Someşul Mic River.

The deuterium analyses of water are carried out on the hydrogen gas obtained by on line quantitative reduction of water sample (about 1 μl) with the home-made mass spectrometer SMAD-1.The deuterium content is expressed as δD values, $\delta D=(R/R_S-1)\ 1000$, where R is the deuterium ratio of sample, and R_S is the ratio of international V-SMOW standard (Vienna Standard Mean Ocean Water). The precision of δD values was ± 2‰.

The $\delta^{18}O$ values were measured by an isotope ratio mass spectrometer type ATLAS 86 designed by Varian. The precision of the $\delta^{18}O$ measurements was ± 0.3‰. The results of the measurements are presented in Fig. 1.

These measurements confirm previous studies (Cuna, Berdea, Baciu, 2001) showing that all the springs are related to a unique aquifer. The waters following different ways to reach the surface in the salt brecia zone reach the surface with different chemical compositions.

The δD vs. $\delta^{18}O$ values of these five springs confirme the meteoric provenience, having the deuterium content of meteoric water, but shifted to higher ^{18}O content. This $\delta^{18}O$ shift is the result of isotopic exchange of the oxygen from water with salted layers in the water trajectory to the descharge.

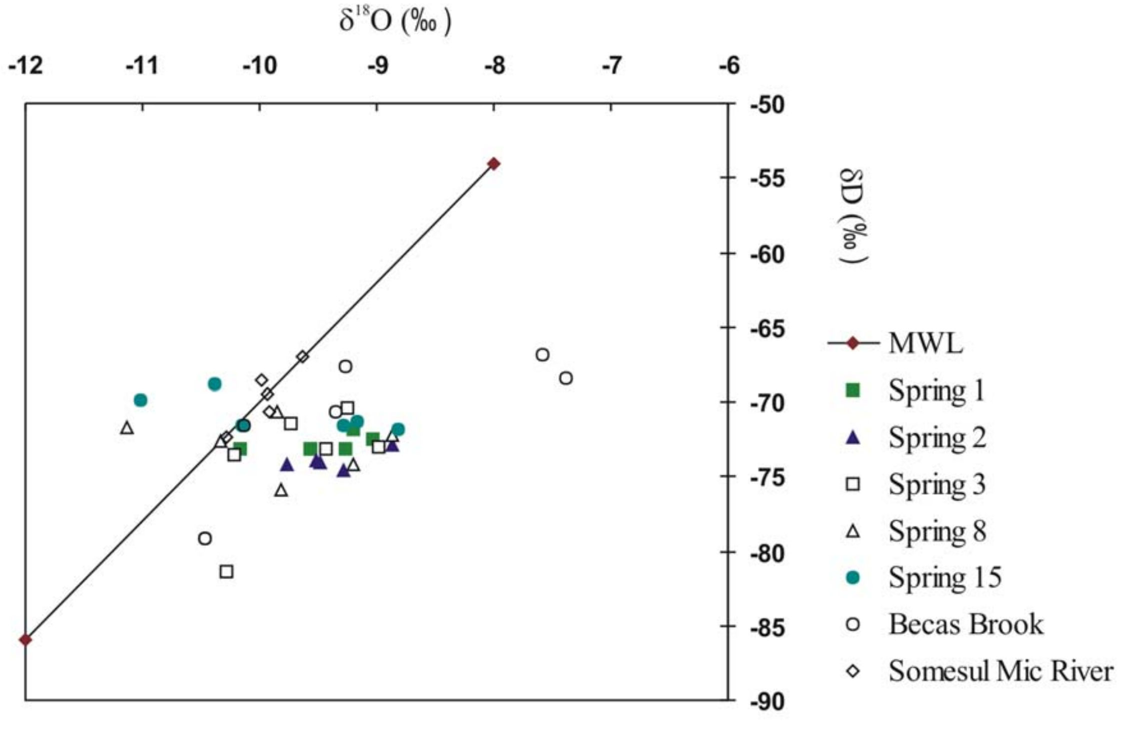

Fig. 1. δD vs. $\delta^{18}O$ in waters from Someşeni Spa area

An inexpected ^{18}O enrichment in Becaş Brook water, probably having the cause in the micro-organisms activity in poluted warm water, was also observed. There are others three inexpected values for the springs No. 8 and No. 15. We have supposed that these values present the water isotopic content of mixed water with shalower meteoric water having heavier isotopic (D, ^{18}O) content. The water from spring No. 3 and from the Becaş Brook show one values with water depleted in D and ^{18}O isotopes. This values is related to the spring time isotopic pulses. That means the spring No. 3 is mixed with Becaş Brook, so this spring is improper for human use.

In conclusion, the isotopic δD and δ^{18}O investigations of the five springs from Someşeni Spa confirme the meteoric provenience having the deuterium content of meteoric water. The values of ^{18}O shifted to higher ^{18}O content confirm the deeper circulation. The waters from springs No.1, 2, can be used as mineral waters. The spring No. 3, 8, 15 are improper for medical use being mixed with shalower waters.

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Introducing a routine LC-IRMS interface Finnigan LC IsoLink: a completely new concept

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With the introduction of compound specific isotope analysis by irm-GC/MS the immediate for similar applications using HPLC was created. In irm-GC/MS the carrier is helium, which does not interfere with the essential combustion step prior to isotope ratio mass spectrometry (IRMS). In opposite the LC mobile phase has inhibited a similar direct conversion up to now. All earlier irm-LC/MS approaches were based on the removal of the liquid phase prior to combustion risking fractionation of the isotope ratios of the eluted compounds. To avoid such restrictions we have developed a new continuous flow concept for the coupling of an HPLC system to the isotope ratio MS.

The differentiation idea of the new concept is to leave the compounds in the effluent and to combust them in the liquid phase. Then separate the resulting CO_2 compound peaks from the effluent and analyze then with the isotope ratio MS.

First results on sensitivity, linearity and precision will be shown. First applications will give an idea on the broad range of possibilities.

Anomalous isotopic composition of carbonates from Quaternary evaporitic deposits, Western Qaidam, China: evidence for thermogenic derived methane

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The Himalayas, the Tibetan plateau and the adjacent mountains north of the plateau, are the most outstanding present-day topographic features resulting from continent-continent collision. The average elevation of the region reaches 4000-5000 meters, the progressive south-north shortening due to collision achieving ca. 1400 km. The Neohimalayan tectonic phase had started during early Miocene, and was followed by accelerated denudation within the past few million years.

The Qaidam basin is located at the northern edge of the Tibetan plateau. The thick Pliocene-Quaternary sediments were monitored by tectonic processes related to uplift of the Tibetan plateau as well as by climatic changes related to the plateau growth. The ca. 120.000 km^2 large, rhomb-shaped Qaidam basin, with unusual thick Mesozoic to Cenozoic sedimentary sequences of 3 to 17 km, is surrounded by the Kunlun/Qimantagh, Qilian and Altyn mountain ranges. Mean surface elevation of the basin floor is ~2700 m, whereas the surrounding mountains as Kunlun-, Altyn- and Qilian Shan reach elevations above 5000 m. Latest interpretations consider the formation of Qaidam basin in response to oblique compression between the left lateral Altyn and Central Kunlun faults.

The present climate represents the driest part during the last 40 ka with mean annual precipitation of 25 mm in the centre of the basin and 50 mm along the border. Mean annual evaporation is ~3000 mm, while annual average temperatures are 2 to 4°C. The landscape is characterised by salt lakes, playas and aeolian landforms. There are still 27 salt lakes occupying an area of approximately 1500 km^2. Playas and the salt lakes as for example Yiliping and Quarhan cover about one quarter of the total basin area.

Stable isotope analyses on carbonates from lake evaporates collected from the non-marine Qaidam basin yield a positive excursion from Pliocene to Quaternary times. The positive shift in $\delta^{18}O$ values between the Pliocene and the Quaternary is interpreted as a climatic change from relatively humid conditions to arid conditions. Such high aridity conditions and a closed lake environment were deduced for Quaternary from other proxies like e.g. the widespread salt-deposits and pollen distribution.

At Dafeng Shan, situated in the western part of the basin, the Quaternary sequences are composed of alternating layers of celestine/dolomite and aragonite/calcite with distinct isotopic compositions. The occurrence of celestine indicates, highly saline fluids, with significant concentration of dissolved sulphate These waters could penetrate in underlying sediments leaching pre-existent carbonates or evaporites. Sr solubility decreases with temperature, so, low-temperature fluids were required for transport. The oxygen isotopic compositions of carbonates vary between +4 and +9‰ (PDB), representing the heaviest measured since now. The extreme high $\delta^{18}O$ compositions support also a strong evaporative, closed lake, where such high salinity fluids could develop. The carbon isotopic compositions of carbonates show a large negative excursion of up to 30‰. Microfabrics, mineralogy as well as isotopic compositions suggest recycling of carbon from thermogenic derived methane.

Acknowledgement

Austrian Science Foundation (Fonds für Wissenschaft und Forschung) is thanked for financial support.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Quaternary exhumation mechanism of the Central Himalayan, evidence from fission track and (U-Th)/He data

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Within the study area in the Goriganga Valley (Kumaon Himalayas, India) between Munsyari and Martoli villages four units, separated by major tectonic lines, are exposed. From North to South these are: a) the Tethys Himalaya (TH), composed of low-grade Proterozoic to Mesozoic sediments juxtaposed along the STDZ on b) high-grade gneisses of the Higher Himalayan Crystalline (HHC). The HHC has been thrust along the Vaikrita Thrust (VT), an equivalent of the MCT over c) micaschists and Proterozoic orthogneisses of the Lesser Himalayan Crystalline (LHC). The Munsyari Thrust (MT), in footwall position with respect to the LHC, represents an imbrication zone incorporating rocks from the LHC and sediments from (d) the Lesser Himalayan Sediments.

Based on zircon and apatite (U-Th)/He and fission track data, we discuss here the final cooling stages of the central High Himalayan Metamorphic Belt. The break in the cooling path marked by 2.5 Ma (U-Th)/He zircon ages north of the South Tibetan Detachment Zone (STDZ) and by 0.5 Ma ages south of it, resulted from Pliocene brittle normal faulting along the reactivated STDZ. Zircon data from the Himalayan Metamorphic Belt show a systematic southward increase of both fission track and (U-Th)/He ages. Within the High Himalayan Crystalline the cooling ages increase from 0.5 to 1.2 Ma, whereas within the Lesser Himalayan Crystalline they increase from 1.0 to 1.7 Ma. Lesser Himalayan sediments have cooling ages between 1.3 and 1.8 Ma. By contrast, apatite cooling ages do not display north-south variations within single crustal units and cluster around 0.4 Ma in the Higher Himalayan Crystalline and around 0.7 Ma in the Lesser Himalayan Crystalline. We consider two different mechanisms to explain the observed age distributions.

(1) During an early of Quaternary extrusion tectonic exhumation was dominant with decreasing rate towards the south. During this phase the recent topography with pronounced break-in-slopes at the major tectonic lines was created. Tectonic exhumation rates exceed erosion rates, leading to the positive slopes of ages in the (U-Th)/He and FT zircon ages.

(2) The uniform apatite cooling ages within the distinct crustal domains are explained by accelerated Quaternary erosion with rates proportional to the slope of the relief.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

Genesis of a Na-Ca rich layer near Traföß: evidence from mineralogical and stable isotope data

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The Traföß ultramafic rocks of the Speik unit are situated on the northeastern edge of the Gleinalm metamorphic core complex. The Traföß ultramafics are serpentinites with antigorite and crysotile as main minerals. Characteristic for these serpentinites are the presence of layered ultramafics with clinopyroxene, olivine and actinolite rich levels (Neubauer, 1988). On the Mur valley, near Traföß, within the serpentinites, a 50 cm thick white-greenish layer occurs. For this unit, it is the only occurrence of this rock type. The green spots are composed by amphibole, chlorite and subordinately pyroxene, the white areas consist of zeolites, feldspar and calcite.

The chemistry of amphiboles indicates that they belong to the actinolite, pargasite/edenite group. The pyroxene is an augite, most probably with a magmatic origin. The white matrix is composed of zeolites and feldspars. X-Ray data indicate the presence of Natrolithe $Na_4Al_4Si_6O_{20}*4H_2O$ and Thomsonite $(Ca,Na,Sr)_{12}(Si,Al)_{40}O_{80}*24H_2O$. Microbeam analyses indicate the presence of Sr-Thomsonite $(Sr_{7,06}Na_{4,34}Ca_{0,50})_{11,90}(Al_{18,44}Si_{21,28})_{39,72}O_{40}*$. World wide, beside Traföß, Sr-Thomsonite has been found only on the Kola peninsula, which is its type locality. In the zeolite matrix, 20 microns large Celsian $(Ba_{0,94}Ca_{0,04}Na_{0,02}K_{0,01})_{1,01}(Al_{1,94}Si_{2,05})_{3,99}O_8*$ inclusions are present. Subordinately, native copper, magnetite, chromite, ilmenite, a silver gold alloy as well as zircon and titanite were put in evidence. The zeolites and feldspars are partially replaced by calcite. The contact to the serpentinite is characterized by the presence of some tenth of centimeter thick zone with amphibole and chlorite.

The isotopic values of antigorite show high δD (52 - 68‰) and low $\delta^{18}O$ values. These values are characteristic for oceanic serpentinites formed at moderate temperature (350°C±50) in the presence of a fluid dominated by oceanic water. As the system evolved during amphibolite facies metamorphism without the participation of an external fluid, the primary ocean floor isotopic signature has been preserved. The δD values of actinolite and chlorite within the transition zone and the green-white layer show lighter values, between -69 to -95‰. These values are interpreted to represent local infiltration of an external fluid during the formation of the metasomatic body. Further investigations on oxygen and carbon isotopic signature of silicates and carbonates are in progress.

Discussions: The described mineral association of the white-green layer is interpreted to represent a metasomatised magmatic layer within the serpentinites. Such metasomatic bodies within the serpentinites are known as rodingite. Generally they are enriched in Ca, and composed of Ca-rich phases as grossular, vesuvian, clinozoizite, Ca-amphibole etc.. In this case, the described metasomatic body is characterized by the presence of Ca- as well as of Na-rich phases. The Sr- and the Ba-contents are also much higher than these of the surrounding rocks. Augite and Chromite are interpreted as the only primary magmatic relicts. Actinolite and chlorite are formed during metamorphism, and replaced during the cooling path with zeolites and calcite. The isotopic signature of serpentinites shows the preservation of the primary signature of an oceanic serpentinite. Local infiltration of an external fluid was responsible for the formation of the metasomatic body. The described rocks display parageneses different to the typical ones for rodinigites or albitites. We propose the following steps for the formation of the above described rocks found at Traföß:

1) Metasomatism of the serpentinite hosted protolith (mafic rock protholit?). The rock was formed under low oxygen fugacity as indicated by the presences of copper. Hydrogen isotopic composition of host rocks is characteristic for oceanic serpentinites formed at moderate temperatures (350°C±50) in the presence of a fluid dominated by oceanic water. As the system evolved during amphibolite facies metamorphism without the participation of an external fluid, the primary ocean floor isotopic signature has been preserved.

2) During regional metamorphism, amphiboles, feldspars and chlorite formed within the metasomatic body. The hydrogen isotopic values, much lower of that of the host rock, are interpreted to indicate local infiltration of an external fluid during amphibolite facies metamorphism. The small actinolite-chlorite-zone between the host rock and the metasomatite could represent an altered serpentinite.

3) During retrograde cooling, the feldspars were replaced by zeolites and finally by calcite. The extensive zeolitisation suggest high fluid availability on the retrograde metamorphic path. The presence of calcite indicate that, at least during the last mineral building

phase the CO_2 fugacity of the fluids was high. The isotopic composition of the calcite supports formation temperatures lower than 100°C.

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Ammonium in Neoproterozoic and Palaeozoic sediment records a tracer for climate changes?

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Focus of our studies was to light up the fate of nitrogen in ancient sediments, where NH_4^+ is the dominating nitrogen species. The ammonium nitrogen in sediments is derived from organic matter. The nitrogen isotopic signature of organic matter depends on the metabolism and is related to the kind of nutrient and its availability as well as the biological production rate. During diagenesis, coupled organic-inorganic geochemical processes result in the mineralization of nitrogen. The formed ammonium may be incorporated in clay minerals. The fixed structurally bonded NH_4^+ is not easily released or exchanged and records the chemistry of the diagenetic environment in the sediments (e.g. Williams et al., 1989, 1991, 1995; Compton et al., 1992; Lindgreen, 1994).

Devolatilization processes of NH_4^+ during regional and/or contact metamorphism decrease the ammonium content and enrich ^{15}N in metasediments (e.g. Haendel et al. 1986; Bräuer et. al. 1990; Bebout and Fogel 1992; Bebout 1997 and Mingram and Bräuer 2001). There has been little work on the distribution of ammonium and its $\delta^{15}N$ values in ancient low metamorphic sediments. Therefore, this study wants to bridge the gap between investigations on nitrogen of early diagenetic sediments and studies of NH_4^+ in metamorphic rocks.

For this reason, the concentration and isotopic composition of NH_4^+-nitrogen and organic carbon have been determined in anchimetamorphic sedimentary sequences from different regions of Central Europe. The pelitic rocks and black shales stem from the Saxothuringian (Thuringia, signed as TH), the NE German Basin (East Avalonia) and from an offshore-borehole in the Baltic Sea (Baltica, signed as G 14).

The stratigraphic units span from Neoproterozoic to Triassic age. Correlations between NH_4^+ and ^{15}N as well as TOC and $^{13}C_{TOC}$ will be presented. About 240 samples were analyzed. The TOC contents range from 0.05 to 24 wt. % and the $\delta^{13}C$ values from -35 to -22 ‰ PDB. The fixed N contents (NH_4^+) range from 50 to 4000 ppm and the $\delta^{15}N$ values vary between -2.4 and 6.6 ‰. NH_4^+- and TOC contents are positively correlated. This correlation does not hold for the black shales. $\delta^{15}N$ and NH_4^+ are inverse correlated due to the relationship between nutrient supply and utilization. The higher the nutrient supply, the lower the $\delta^{15}N$ values.

A clear inverse correlation was found between $\delta^{15}N$ and $\delta^{13}C_{TOC}$ of the G 14 samples deposited under strictly marine conditions. A similar trend can be seen in the TH sediments if the Neoproterozoic samples are excluded.

Finally, it should be proved whether sedimentary $\delta^{15}N$ has the potential to track early changes in nitrogen cycle and past climate changes. The high TOC contents of the Cambro-Ordovician and Silurian black shales are more caused by the extremely low redox potential than by unusually high biological production. In contrast to that the Lower Carboniferous TOC rich sediments were a consequence of a high biological production rate and evolution of live forms.

The ^{15}N isotopic signature of the mineralized organic matter could be preserved by the NH_4^+-incorporation in clay minerals, but only if the supplied clay minerals are able to recrystallize. Detrial clay minerals deposited under arid climate conditions offer little possibility for K/NH_4^+ exchange.

Nitrogen isotopes provide a useful tool to evaluate the nitrogen consumption in relation to its biogeochemical cycle and the palaeoclimatical situation.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

Holocene and Late Pleistocene climate record of a sub-Mediterranean continental environment, recorded by a stalagmite from Poleva Cave (Southern Carpathians, Romania)

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In the past years, an increasing number of papers have been made use of speleothems as paleoclimatic indicators by measuring the stable isotopes (usually $\delta^{18}O$ and $\delta^{13}C$) variations along their axis. These are considered to reflect variations in mean annual surface temperature (e.g. Gascoyne et al., 1980), and/or the changes of the continental ice volume or long-term shifts in moisture sources (Lauritzen & Lundberg, 1999; McDermott et al., 1999). The development of the U-series TIMS dating techniques often allowed very accurate time-calibrations of such profiles. Since the supply of percolation water (and thus, speleothem deposition) is generally prevented both during very cold or very warm climatic episodes, it appears very likely that speleothems formed either at northern latitudes (e.g. in the sub-Arctic) or southern latitudes (e.g. the Mediterranean) may only preserve incomplete records of the climatic variations. This study have focused on a speleothem (stalagmite PP10) collected from a cave located in the sub-mediterranean region of SW Romania, reasonably far from the influence of the NW Europe (Atlantic) circulation and also from the arid conditions of the SE Mediterranean.

A preliminary U-series alpha-spectrometric date of the base yielded an age of 61.7±11 ka with relatively high error due to the low Uranium content (~0.05 ppm) of the sample. Seven high-resolution TIMS-dates yielded ages in correct stratigraphical order, ranging from ~48 ka to ~3 ka with typical analytical errors of 1–2% (2σ) for ages younger than 15 ka. Along the speleothem axis, 154 stable isotopes samples were analyzed for $\delta^{18}O$

and $\delta^{13}C$. The time-resolution of the sampling corresponds to ~ 2 ka/sample for the lower part of the stalagmite (slow-growing) and to ~150–40 years/sample for the upper (candlestick-like) part. This high resolution has enabled the identification of several clear-marked, rapid, climatic oscillations during the last 12,000 years.

The isotopic profile of the *lower part* of the stalagmite reveals several climatic oscillations during Marine Isotope Stages (MIS) 4 and 3, which are well-documented from other continental and marine records, such as the deglacial event at ~54 ka, an important glacial event between *c*. 47 and 41 ka, and the marked warming between ~ 32 and 28 ka (Denekamp).

The *upper part* of the stalagmite has delivered a detailed oxygen isotopic profile over the last 12 ka, recording several important rapid oscillations that may be correlated globally. The cooling event at ~8.2 ka (Alley et al., 1997) is clearly marked. A general trend of climate warming (including rapid variation episodes with amplitudes as large as ±1,5‰) then follows, culminating with two spikes at ~5.2 and ~3.2 ka. Overall, the isotopic profile recorded by stalagmite PP10 during the last 10,000 years is consistent with the one recorded by stalagmite PP9 form the same cave and reported by Constantin et al. (2001). The warm 3.3 ka-event seems to have a regional extent since it is clearly recorded, with roughly the same amplitude, in both stalagmites from Poleva cave and in PU2 stalagmite from western Carpathians (Onac et al., 2002) — a region that lies under the Atlantic climatic influence.

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New data on the chronology of the Second Termination based on the isotopic study of a stalagmite from Closani Cave (South Carpathians, Romania)

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The stalagmite C6 from Closani Cave (Southern Carpathians, Romania) was accurately dated by U-series thermal ionization mass-spectrometry (TIMS) method. The eight dates showed that the speleothem grew continuously between *c*. 183 ka and *c*. 39 ka. The highest growth-rate was recorded between the base and *c*. 103 ka, allowing a high resolution of the isotopic sampling for the time-range corresponding to MIS 6 to 5c. The isotopic profile (40 samples) is representative for the transition to the Eemian in Romania and shows that the onset of the 2nd Termination may be placed as early as 155 ka, well in advance of the SPECMAP chronology. A short and rapid cooling recorded at *c*. 132 ka suggests that the deglaciation may have been followed the "two-step" pattern known for the Zeiffen-Kattegat episode. As compared with the LFG profile from Litophagus cave in the Western Carpathians, the climatic oscillations corresponding to interstadials 5d and 5b appear surprisingly large, indicating that the Carpathian Range acted as a barrier between two different sources of atmospheric circulation on the Romanian territory.

Carbon isotopic variations in species of lichens on an altitude gradient in the South Carpathians and Apuseni Mountains, Romania

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In the present work, the natural isotopic variations of $^{13}C/^{12}C$ in lichens are analyzed in relation to an altitude gradient, to different collection dates, and to different photobiont associations. We have studied the lichens because they are extremely sensitive symbiotic organisms consisting of a fungus (mycobiont) and an algae or cyanobacterium (photobiont) which might react to even slightly polluted air. Lichens are biomonitors with a good accumulation capacity that allow the determination of pollutants deposition in terrestrial ecosystems (Catarino et al., 1991; Nimis et al., 2001).

The lichen species studied were Cladonia., Peltigera canina, Hypogymnia physodes and Pseudovernia furfuraceea. These lichens were collected in Retezat Mountains, Hăşmaşu Mare Mountains and Bihor Mountains, Romania. The colelction of data was performed during 1978, 1987, 1989, 1994 and 2003. The carbon isotope composition ($\delta^{13}C$) in organic material from 56 lichen samples has been measured. The lichen samples were combusted to obtained CO_2 for isotopic analysis. CO_2 was purified on cryogenic traps and then analyzed by a dual-inlet isotope ratio mass spectrometer, model ATLAS designed by Varian. The mean standard deviation is ± 0.3‰.

The results show that the $\delta^{13}C$ values for all studied lichens variy between –21.21‰ and –26.93‰, in the range normally associated with C_3 higher plants (Ehleringer, 1991).

The studied lichens can be separated into two groups on basis of the type of photobiont partner: phycobiont (like Hypogymnia physodes) where the photobiont is a green algae, and cyanobiont (like Peltigera canina) where the photobiont is a cyanobacteria. We have found a difference between $\delta^{13}C$ of the two groups: the Peltigera canina lichens collected in Bihor Mountains in 1978 showed a mean $\delta^{13}C$ value of –23.67 ‰, and the Hypogymnia physodes collected in the same site and the same date showed a mean $\delta^{13}C$ value of –22.71‰. The difference can be explained by the differences in photosynthetic rates (Maguas and Brugnoli, 1996). The lichens possessing different photobiont associations show different water requirements for the activation of photosynthesis. The cyanobiont lichens require liquid water for photosynthetic CO_2 assimilation, while the phycobiont associations can fix CO_2 in the presence of water vapor. Such differences are related to variation in CO_2 diffusion resistance from air to chloroplasts.

We found a variation of the $\delta^{13}C$ values in lichens with altitude. For Hypogymnia physodes lichens this gradient was from –21.21‰ at 1130m to –26.09‰ at 1520m. We have supposed that the lichens along an altitude gradient are exposed to numerous natural and man-made stress factors and react sensitively to any pollution. The stress factors have a direct or indirect effect on photosynthetic apparatus of lichens, and as a result on the $\delta^{13}C$ values.

Also, the $\delta^{13}C$ values of the lichens that were collected at different dates showed a gradient. The Cladonia lichens collected in Big Hasmasu Mountains in 1989 year have $\delta^{13}C$ = -21.52‰ and the Cladonia lichens collected in the same mountains, but in 2003 year, have $\delta^{13}C$ = -24.75‰. The Pseudovernia furfuraceea lichens collected in the same mountains in 1989 have $\delta^{13}C$ = -23.29‰, and the Pseudovernia furfuraceea lichens collected in 2003 have $\delta^{13}C$ = -25.03‰. All these lichens were collected at the same altitude. The ^{13}C content from organic material of these lichens is depleted in the lichens collected in 2003 year in relation to the lichens collected in 1989.

For both species, a decrease in $\delta^{13}C$ values was associated with the change in the $\delta^{13}C$ and CO_2 concentration of the CO_2 atmospheric after a lapse of 14 years. This evidence is relevant for understanding the impact of global change on natural vegetation.

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Stable isotope and noble gas isotope compositions of inclusion fluids from Larderello geothermal field, Italy

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In the steam-dominated field of Larderello two distinct geothermal reservoirs have been identified: a mostly sedimentary (limestones, shales, slightly metamorphosed sandstones) shallow reservoir, and a metamorphic (phyllite, micaschist, gneiss, granite) deep-reservoir. Both produced superheated steam, consisting of different proportions of meteoric, metamorphic and magmatic water components. Fluid inclusion studies on quartz from hydrothermal veins, contact-metamorphic assemblages and granites documented the circulation of several fluid types during the geothermal activity. The first hydrothermal stage was dominated by aqueous-carbonic fluids, formed during contact-metamorphism, and Li-Na-rich brines of magmatic derivation. The late stage hydrothermal activity was charcaterized by the circulation of meteoric-derived aqueous and aqueous-carbonic liquids, vapour produced during boiling processes, and saline fluids related to evaporite/fluids interaction. In addition, inherited quartz veins in metamorphic formations may also contain fluids trapped during regional metamorphism and, therfore, not related to the geothermal activity.

Stable isotope investigation of minerals and fluid extracted from inclusions, formed during different periods of time, has been used to constrain the nature of fluid-rock interaction processes at Larderello. In situ laser-fluorination of quartz-dominated veins revealed marked difference in the $\delta^{18}O$ values of primary (metamorphic) and/or secondary (recrystallized lenses in the metamorphic assemblage) quartz, varying from 13.4 to 14.0 ‰, and from 6.0 to 8.4 ‰, respectively. Fluids extracted from thermally decrepitated inclusions have δD values of from –52.9 to –85‰ and indicate that the fluids were derived from mixing of water-rich components, likely a surface reservoir similar in composition to present day meteoric waters, and a deep reservoir. A deep source of He contribution at Larderello is suggested by R/Ra ratios (up to 3.2) of paleofluids and present-day fluids.

The fluids trapped in texturally late fluid inclusions show N_2/Ar and $^{40}Ar/^{36}Ar$ ratios as low as those of air saturated water, similar to present-day geothermal fluids, whereas early stage fluids are characterized by excess radiogenic Ar and high N_2/Ar ratios, likely resulting from the circulation of fluids during contact metamorphism subsequent to the emplacement of granitoid rocks, and from devolatilisation of basement rocks. The $\delta^{13}C$ values for CO_2 from the early stage fluid inclusions were produced by carbonate country rock devolatilization; $\delta^{13}C$ values as low as -17 ‰ were measured in late stage fluid inclusions, likely produced by oxidation of organic matter at shallow depths.

Permian-Triassic boundary events in continuous marine successions in Hungary

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In continuous marine successions the Permian-Triassic boundary was recognised in several outcrops in the Bükk Mts, North Hungary and in a few core sections in the NE part of the Transdanubian Range.

Although rocks in the Bükk Mts (sampled at the „Bálvány section") has been affected by very low-grade metamorphism, the sections are still well preserved. It is reflected in the preservation of the original sedimentary features and even fragile thin-shelled fossils. The topmost Permian is made up of dark grey limestone, rich in fragments of crinoids, calcareous algae, mollusks, brachiopods, ostracods, foraminifera. There is a dramatic decrease in the amount of the bioclasts in the last two limestone layers that are overlain by a 1 m thich shale bed. The lower two third of this bed still contains a poor biota but its upper part is almost free of any bioclast. The overlying platy limestone contains a poor fossil assemblage indicating stress conditions.

The $\delta^{18}O$ values are fairly constant at –7 ± 0.5 ‰ in the whole section. In contrast, the carbon isotope compositions show systematic variations up-section. In the limestone layers 1.5 m below the base of the shale, the $\delta^{13}C$ values are about +3 ‰. Preceeding the complete disappearance of Permian fossils the $\delta^{13}C$ values start to decrease gradually, reaching –0.5 ‰, in the lower part of the shale bed, then they suddenly drop below –4 ‰ just at the second biotic decline. After the sharp negative peak the $\delta^{13}C$ values recover to 0 ‰ and stay constant at cca. –1 ‰. The observed change show no relationship with lithology as reflected by the carbonate content. Thus, the observed variation is not related to formation of diagenetic or metamorphic carbonate and can interpreted as a primary signal.

The isotopic signature of the Bálvány section resembles other well-preserved sections worldwide. However it differs significantly from that in the Transdanubian Range where the boundary was found in ooidic limestone akin to that in that in the Southern Alps (Tesero Horizon). In these sections $\delta^{13}C$ values show gradual decrease and there is a slight $\delta^{13}C$--$\delta^{18}O$ correlation, but the definite negative $\delta^{13}C$ peak is missing. This feature may either be related to primary or secondary causes. Based on literature data, the primary cause can be the changing magnitude of $\delta^{13}C$ shift depending on facies and latitude. Secondary causes can be sedimentary or diagenetic. The influence of diagenesis is supported by the weak $\delta^{13}C$-$\delta^{18}O$ correlation, whereas sedimentary reworking – and thus smoothing the negative $\delta^{13}C$ peak – is indicated by Permian fossils enclosed in ooides in lower Triassic layers.

The strong and symmetric $\delta^{13}C$ peak at the second biotic decline observed in the Bálvány section (Bükk Mts., North Hungary) indicate a rapid process that contributed to the ocean–atmosphere system with a huge mass of ^{12}C followed by system recovery at the same rate. The most plausible explanation is release of methane hydrate from deep sea sediments due to rapid warming, then rapid cooling and hydrate formation that removed the excess ^{12}C from the system. The gradual and long term $\delta^{13}C$ shift from Permian to Triassic $\delta^{13}C$ values (from +3 to –1 ‰) would indicate a collapse and incomplete recovery of the organic productivity.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

Isotope hydrological study of soil salinization in a sodic grassland on the Hortobágy, Hungary

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Introduction

The lowest part of the Carpathian Basin is the Great Hungarian Plain (GHP) with an average elevation about 100 m a.s.l. Many regional groundwater flow system has its discharge area on the GHP, where the annual rate of evaporation exceeds the amount of precipitation. As the result of this negative water balance salt, originally carried by the old groundwater, accumulates in the soil horizon causing problems for the agricultural activity.

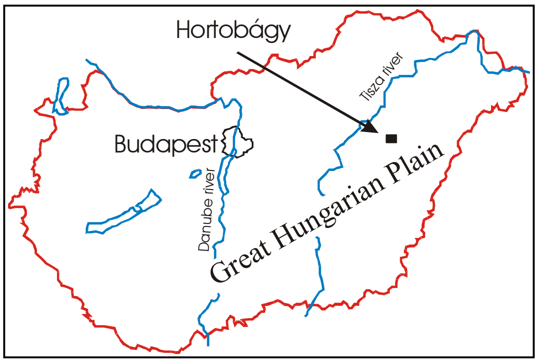

Fig. 1. The sketch map of Hungary with the indication of the studied area.

One of the most characteristic native sodic grassland of Hungary, the Nyírőlapos, a small area of 600x800 m site on Hortobágy (Great Hungarian Plain, Fig. 1) was selected for studying the salt accumulation in the soil by different methods: water level observation, soil bulk electrical conductivity (EC_a), water chemistry, and stable oxygen and hydrogen isotope analyses.

In this presentation mostly the stable isotope data will be evaluated with reference to the salt accumulation. The evaluation of time series of EC_a data has been published elsewhere (Tóth et al. 2002).

Results and interpretation

Water samples were taken from monitoring wells at 9 points in every month for chemical analysis. During the sampling campaign of 5 June 2002 water samples were taken for stable isotope measurements as well. At five out of nine points three wells were installed for monitoring water at different depths. The bottoms of the shallowest wells are at two meters below the water table (usually 3-4 meters below the ground surface). The bottoms of the medium deep wells are at about 6 meters below the ground surface, and the bottoms of the deepest wells are at about 10 meters below the ground surface.

The stable hydrogen and oxygen isotope data are shown on Fig. 2. The points are distributed along a line of $\delta D = 7.4953*\delta^{18}O - 0.949$, which is under both the Global Meteoric Water Line (GMWL) and the Groundwater Line of the Carpathian Basin (CGWL). The slope of the line (7.5) is a little bit lower then 8 indicating the effect of the local evaporation. The delta values vary in a wide range (δD -85.5‰ to -58.4‰; $\delta^{18}O$ -11.18‰ to -7.59‰). The $\delta^{18}O$ value of the infiltrating water in Hungary is -9.3± 0.4‰ (Deák et al. 1996), so $\delta^{18}O$ values of ≥ about -8.8‰ indicate heavy isotope enrichment by evaporation. Usually these latter samples have the highest TDS (total dissolved solids) values. At the other end of the line the $\delta^{18}O$ values are more negative then those infiltrated during the Holocene era (<-10‰), so these very negative $\delta^{18}O$ values may indicate water infiltrated during the latest glaciation. The studied area is a discharge area of a regional flow system, whose recharge area is the karstic Bükk Mountains north of Hortobágy. The $\delta^{18}O$ values of the ascending water nearby the studied area are between -11.5‰ and -11.8‰ in the depth range of 30-60 meters, which clearly indicates that this ascending water was infiltrated during the Ice Age. Stute & Deák (1989) published δD and $\delta^{18}O$ data for the deep groundwater circulation systems under the GHP (see Fig. 2). It is interesting to notice that the majority of these points are distributed along the CGWL, but some of them appear around the water line of the studied area, mostly those with $\delta^{18}O$ values of < -10.5‰. This fact that deep, undisturbed groundwater samples show up under the GMWL may be explained by two reasons. 1) The water infiltrated from a precipitation which originated from a place where the relative humidity of air was high, or 2) the infiltrating water suffered evaporation effect during the infiltration. Both can be imagined during the Ice Age, because the climate was cold and dry.

The water line of the samples of the studied area is a mixing line, where the old ascending water mixes with the infiltrating water from the modern precipitation.

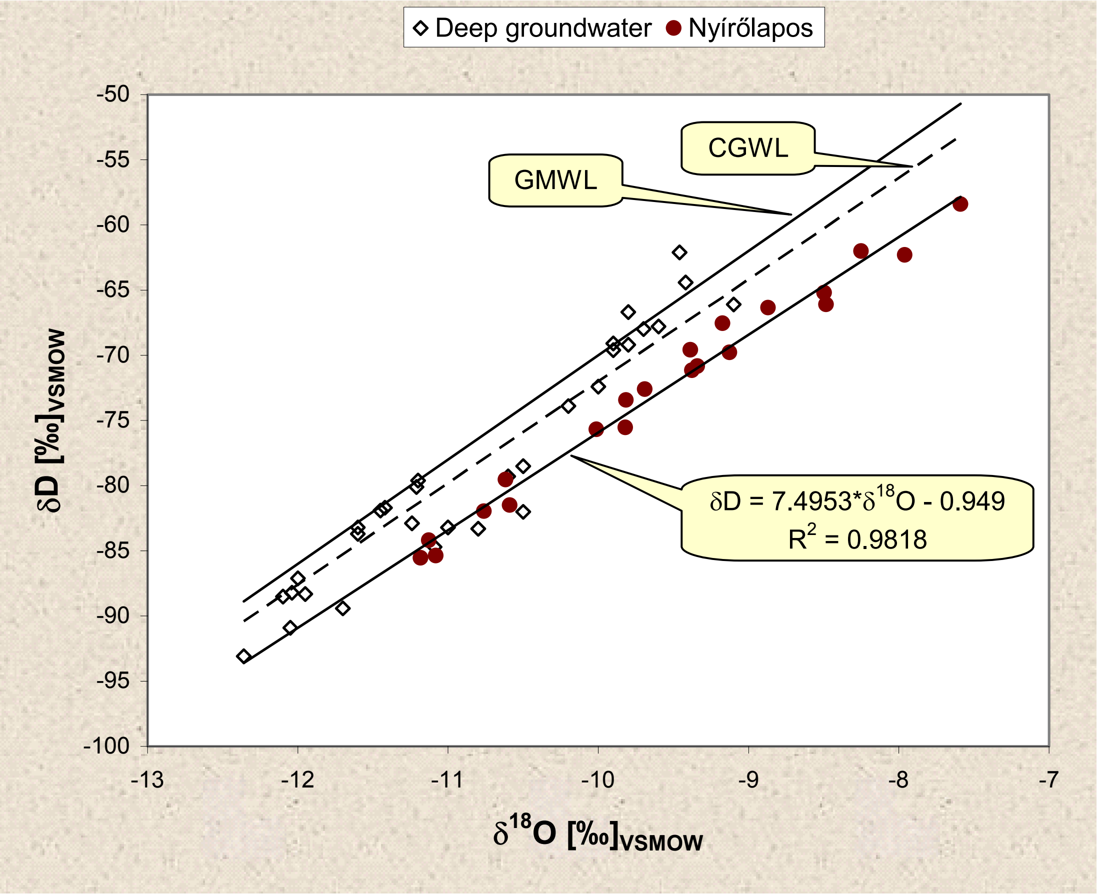

Fig. 2. The δD-δ^{18}O plot of the water samples from Nyírőlapos (solid symbols), and of deep groundwaters from different part of the Great Hungarian Plain (open symbols, Stute & Deák 1989). GMWL = Global Meteoric Water Line δD = 8*δ^{18}O + 10 ; CGWL = Groundwater Line of the Carpathian Basin δD = 7.8*δ^{18}O + 6, Deák 1995).

The spatial distribution of mixing ratio is not homogeneous, see Fig. 3. The flux of the up-welling water is maximum, where the permeability of the alluvial sedimentary layers is highest, e.g at about the 5100-9900 m relative coordinates (Fig. 3). At some sites the δ^{18}O values of the deeper water samples are less negative than that of the shallowest one, while at other sites this relation is the opposite, indicating a very complex mechanism of the mixing process.

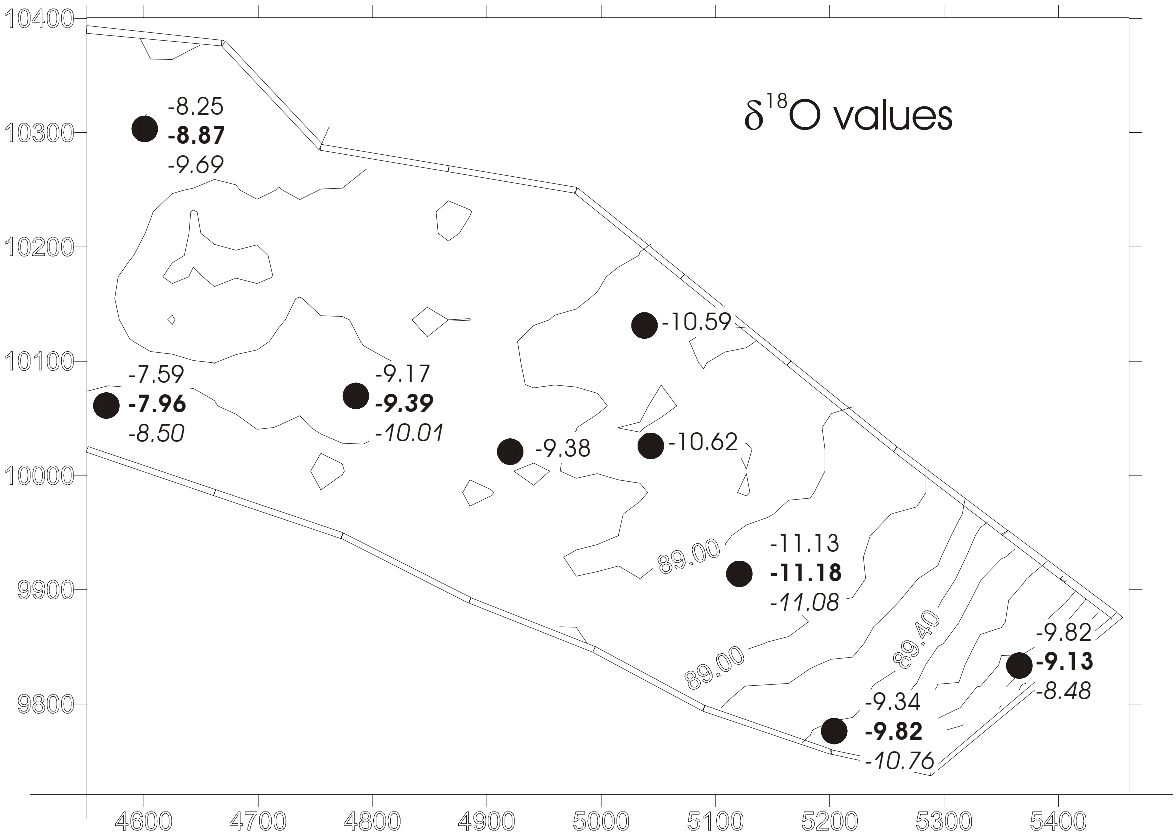

Fig. 3. Elevation map of the studied area, Nyírőlapos. The x and y axes are relative positions in meters along the West-East and South-North directions. The δ^{18}O values of the water samples are indicated. At those sites, where there are three numbers, the first one is the δ^{18}O value of the shallowest well (3-4 m from the surface), the second number (in bold) is the δ^{18}O value of the medium deep well (6 m below surface), and the third number (in italic) is the δ^{18}O value of the deepest well (10 m below surface). Where there is only one number it refer to the shallowest well.

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Contrasting origin of fluids during Late Cretaceous deformation, Eastern Alps, Austria: evidence from stable isotopes, fluid inclusions and microfabrics

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The Eastern margin of the Graz Thrust Complex (Eastern Alps) represents a major late Cretaceous extensional fault zone where high-grade lower structural units (Middle Austroalpine) are juxtaposed against low-grade higher structural units (Upper Austroalpine). Approximately coeval to overall NW-SE extension the late Cretaceous Gosau molasses type basin developed (Neubauer et al., 1995; Ebner and Rantitsch, 2000). Extension tectonics and exhumation of rocks resulted in formation of an extremely disturbed and condensed metamorphic field gradient. Over a distance of 3 kilometres metamorphic conditions for the Late Cretaceous decrease from ca. 550°C and 10 kbar down to surface conditions. During exhumation of rocks close to surface levels a change from metamorphic to meteoric fluid regimes as well as a change in fluid pathways is expected. We elaborated structural and stable isotope data to put constraints on this scenario.

he general geology of the area comprises from structural footwall to hanging wall the following units: (1) The Middle Austroalpine Koralm Basement to the west and the Gleinalm Basement to the North are composed of amphibolite facies metamorphosed metapelitic rocks intercalated by marble beds, amphibolites and pegmatites. (2) Upper Austroalpine Nappes of the Graz Nappe Complex constitute carbonates of Lower Paleozoic age that are (3) transgressively overlain by terrestric to shallow marine Gosau type sediments. The contact between Graz Nappe Complex and Gosau is highly brecciated and fluid infiltrated. Several generations of reddish carbonates precipitated within veins and voids. The reddish colour is result of hematite pigmentation.

Oxygen and carbon isotope data measured systematically from Middle Austroalpine marble beds into to metapelites gave an asymmetric "bell shape" geometry indicating limited fluid exchange across lithological boundaries. Models of fluid rock interaction suggest major lateral flow of metamorphic fluid mainly parallel to lithological boundaries.

Fluid inclusion data show that an early CO_2 dominated fluid was later replaced by and aqueous fluid type with considerable amount of NaCl.

From the brecciated Upper Austroalpine carbonates we elaborated Carbon and Oxygen isotopic data form different types of newly precipitated carbonates. A trend from fresh greyish carbonates to highly infiltrated reddish ones show systematic decrease in $\delta^{18}O$ from 26 to 16 and $\delta^{13}C$ from 2 to –6.

In summary the following scenario of fluid rock interaction during late Createaceous extension and exhumation of rocks is proposes.

(1) Within deeper crustal levels predominatly CO_2 rich metamorphic fluid circulated parallel to major lithologic boundaries.

(2) At higher crustal levels the original Devonian carbonated were infiltrated by Createaceous marine and meteoric water.

(3) The isotopic signature was modified by CO_2 degassing during decompression.

(4) Highly oxidising fluids enabled precipitation of hematite

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Isotope Investigations of thermal waters in the Pannonian Basin, (SE) Hungary

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The Pannonian basin is located in eastern Central Europe encircled by the Eastern Alps to the west, the Western Carpathians to the north, the Apuseni Mountains to the east and the Dinarides to the south. Its formation began in the early to mid-Miocene accompanied by intense volcanism, E-W crustal extension, and local block faulting. In the basin, which still exhibits heat-flow anomalies, there are a lot of thermal springs containing large volumes of carbon dioxide and/or hydrocarbon gas.

H and O isotope ratios and H and C isotope ratios of methane as well as the abundances of some major and minor dissolved components were measured earlier (Vető et al, 2004) in 26 subsurface waters from SE Hungary, produced from late Neogene aquifers within the upper two kilometers in depth. From the isotope data Vető et al. concluded that about two thirds of the waters are dominated bacterial methane produced during early burial. In the corresponding aquifers methanogens started to operate immediately after the sulfate content dropped below 0.1 mmol/l due to bacterial sulfate reduction. In about one third of the waters bacterial sulfate reduction was inhibited by some unknown mechanism and, with continuing burial, the corresponding aquifers became sites of intensive bacterial acetogenesis and subsequent fermentation of the acetate to methane in the depth interval of about 600–1000 m at temperatures of about 40–60 °C (Vető et al, 2004).

For the better understanding of the governing mechanism the former isotope studies were completed with $\delta^{13}C$ measurements of dissolved inorganic carbon (DIC) and of the co-existing CO_2 gas, as well as $\delta^{15}N$ study of the dissolved ammonia. On the basis of parallel $\delta^{13}C$ (CO_2) and $\delta^{13}C$ (CH_4) data we could identify gases originating from saline carbonate reduction or methyl fermentation. These isotope investigations help to interpret the water isotope data ($\delta^{18}O$ and δD) and understand the origin of waters.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Comparison of total uncertainty in off-line dual inlet and online continuous flow IRMS measurement of ^{13}C in organic solids

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The stable isotope of carbon, ^{13}C, has a broad field of applications. Generally the measurement of this isotope is done in a differential way, which means comparison to a reference material for which a value was adopted. Expression of results in this technique, isotope ratio mass spectrometry, is illustrative of this way of working, since the delta-value in per mill is based on the relative difference of isotope ratios of the substance under study and a reference material. Within IRMS different techniques are possible: on the one hand dual inlet, in which the gas to measure and the reference gas are admitted through each side of a double inlet system and subsequently measured repeatedly; on the other hand continuous flow in which conversion of the sample to the gas suitable for IRMS measurement is done online with the IRMS and one actual measurement of the sample takes place. In the latter a carrier gas assures transport of the gases continuously from conversion module to mass spectrometer. Hence “continuous flow” (CF).

Switching to CF was a step forward in many respects. However, it should not mean the creation of a larger uncertainty in the total process of ^{13}C measurement. This study is aiming to assess the uncertainty involved in CF-IRMS for the measurement of ^{13}C in organic solids, as compared to uncertainty in the dual inlet technique, the latter including off-line sample preparation. Uncertainty statements play a major role in the establishment of transparency of the value assignment process. Knowing the major sources in an analytical procedure is of major importance, since this is the first step in optimisation of the value assignment process.

In the estimation of the total uncertainty of IRMS ^{13}C measurements for organic solids several components are present. Off-line preparation of different nature (CO_2 phosphoric acid liberation in case of carbonates, EA-combustion of organic solids) of reference materials and samples, the use of secondary reference materials and the mass spectrometric measurement yield different uncertainties in the different techniques, i.e. off-line EA-dual inlet IRMS and CF EA-IRMS. In this study uncertainties are shown for the off-line preparation of CO_2 from organic solids using elemental analysis equipment, followed by dual inlet IRMS and online measurement in EA-IRMS of organic solids.

C and S isotope variations in solid atmospheric particles and sulfate in precipitations in Wrocław (SW Poland).

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Introduction

In spite of tremendous improvement of the air quality in the last 10 years, the problem of clean air is still crucial in large city. Two types of the environmental atmospheric pollutants are usually discriminated: 1) *low emission* (from the local home hearths and traffic pollutants) and 2) *high emission* (from the large industrial plants). This work describes the results of solid atmospheric particles and rainwater sulfates studies in Wrocław downtown (SW Poland). The samples analyzed, were collected into12 passive collectors (Jires et al. 2001) in Wrocław, where old type of buildings, showing the *low type emission* and traffic pollutants, predominates. Basic problems of air quality in Wrocław have been described by other authors (e.g. Drzeniecka et al. 2000, Jędrysek 2000, 2003, Mikołajczyk et al. 1999).

The major goal of this work was: 1) to determine participation of the one local large pollutants emitter (heat and power station "Wrocław") in the atmospheric pollution mass balance in Wrocław; 2) detect the potential zonation with respect to atmospheric pollutants. Carbon and sulphur isotope analysis of solid organic atmospheric particles ($\delta^{13}C$) and sulfate in precipitation ($\delta^{34}S(SO_4^{2-})$) respectively, have been carried out. The isotope analyses have been complemented by meteorological data.

Analytical procedures

The passive collectors were located onto two radiuses at a 1 and 3 km distains from large local pollutants emitter (heat and power station). Each collector was 2,5 m high and had 0,0398 m^2 of the collecting surface. They were installed in November 2003, and this work shows the results of 2 months collection period (one sampling action). Before carbon isotope analyses, the dust material has been dried and washed out with 0,3M HCl (1 hour) in order to remove other carbon phases (mainly carbonates and hydroxides). The total dust fall, separately mineral and organic one expressed in mg/m^2/day. The sulfate in precipitation is shown as SO_4^{2-} deposition in mg/m^2/day.

The organic dust particles were combusted, using cooper oxide (CuO) wire, under vacuum at 900 °C. The CO_2 obtained was cryogenically purified and collected to pyrex ampoules. The $BaSO_4$ were reacted with V_2O_5 reagent, according to the method of Yanagisawa and Sakai (1983). The SO_2 obtained was cryogenically purified and collected to pyrex ampoules.

C and S isotopic ratios were analyzed using the mass spectrometer MI-1305 with special device for nano-mole gas analysis (UMCS, Lublin) and Finnigan Mat Delta E mass spectrometer (Laboratory of Isotope Geology and Geoecology ,UWr, Wrocław).

Results

The geochemical and isotopic data obtained for period 20.01.2003-13.01.2004 as follows:

- the SO_4^{2-} deposition varies between sample points from 0,05 to 1,85 [mg/m^2/day];
- the deposition of total dust varies from 4,53 to 38,04 [mg/m^2/day];
- the deposition of organic particles varies from 3,32 to 15,02 [mg/m^2/day];
- the deposition of mineral fraction varies from 1,20 to 25,44 [mg/m^2/day];
- $\delta^{13}C$ value of organic particles in the dust varies from -25,04 to – 26,02 ‰;
- $\delta^{34}S(SO_4^{2-})$ value in precipitation varies from +6,36 to +13,12 ‰.

Discussion

A positive correlations between total dust fall and mineral fractions (R^2=0,89) and between the deposition of the dust mineral particles and SO_4^{2-} depositions (R^2=0,79) might be explained by the nucleation role of atmospheric dust particles in formation of SO_4^{2-}-rich droplets of precipitations. Increasing dust in air resulted in increasing frequency of precipitations and in consequence to increasing SO_4^{2-} depositions.

It has been observed a zone with preferential deposition of both dust fall and SO_4^{2-} on the direction SW-NE (Fig.1 and 2). This is in agreement with highest velocity of winds but perpendicular to highest frequency of predominant winds .

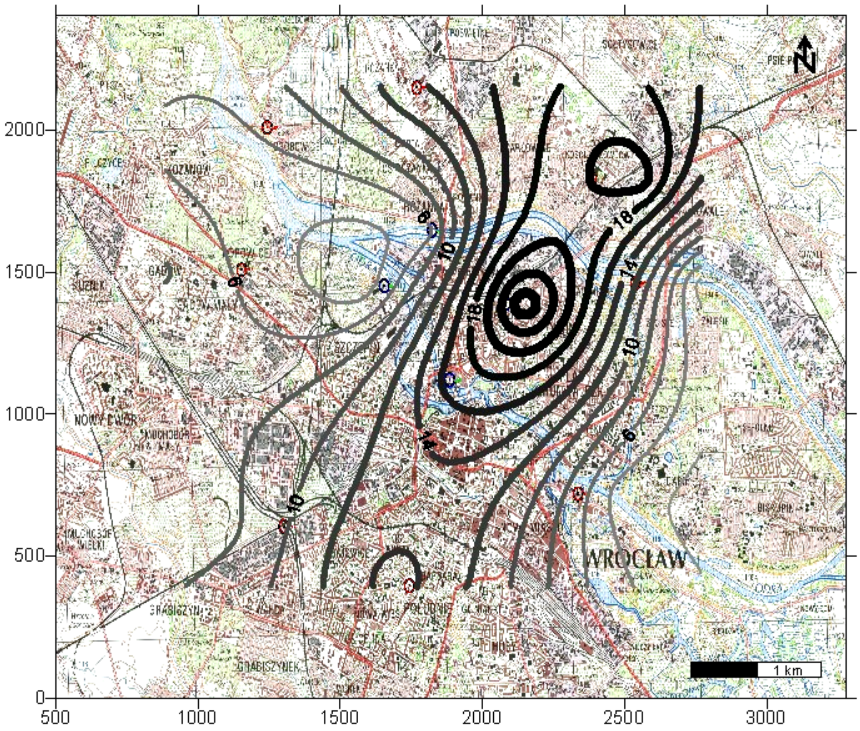

Fig. 1. Distribution of mineral fractions of dust fall [mg/m^2/day] in Wrocław (20.11.2003-13.01.2004).

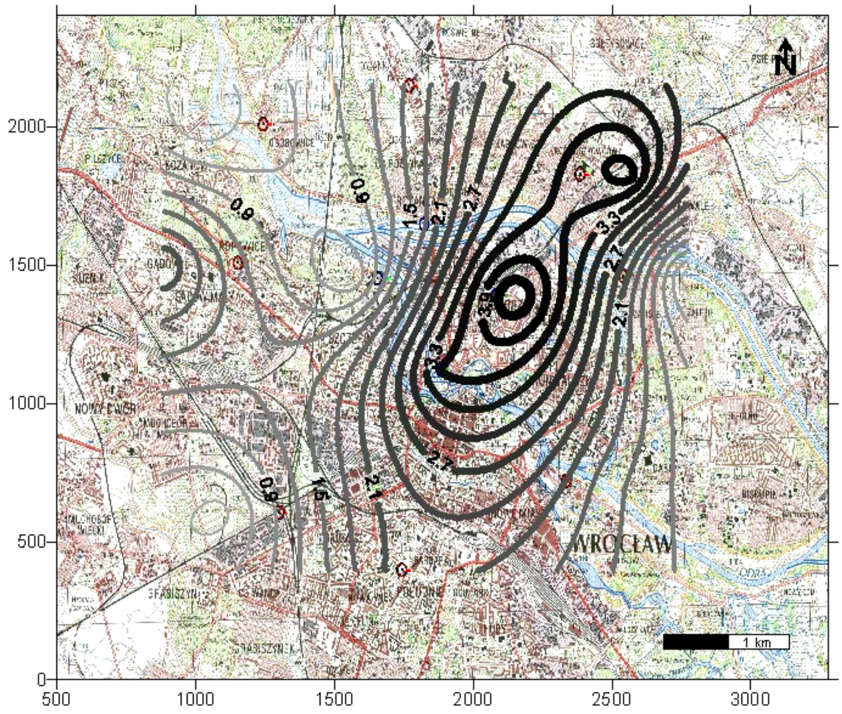

Fig. 2. Distribution of SO_4^{2-} deposition [mg/m^2/day] in Wrocław (20.11.2003-13.01.2004)

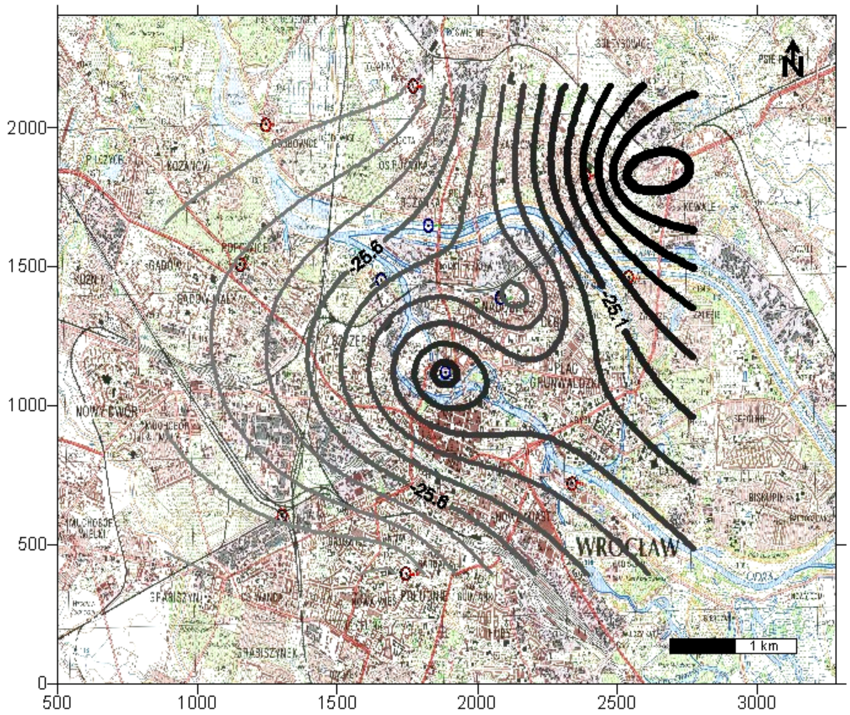

Fig. 3. Spatial distribution of δ^{13}C value of organic particles in the dust in Wrocław (20.11.2003-13.01.2004).

Carbon isotope analysis of organic dust particles indicated two regions of Wrocław with the highest δ^{13}C values (Fig. 3). These regions shows the predominant low air pollutant emission.

Unusually high δ^{34}S(SO_4^{2-}) value has been observed as compare the data obtained earlier in the Wrocław downtown (Jędrysek 2000, 2003). We do not know the reason of this and further investigations will be carried out.

Conclusions

The presented results indicate several type of sources of air pollutants in investigated part of Wrocław downtown. The preferential dust and precipitation sulfates deposition are regions with old compact settlement (low air pollutant emission). In contrast to velocity of wind the role of the predominant wind direction in spread of pollutants is not important factor.

Acknowledgements

Meteorological data have been obtained from Meteorological Observatory of Wrocław (Section for Meteorology and Climatology, Wrocław University). Great thanks are due to Dr A. Kałużny for help in field works.

This study was supported by 1017/S/ING/03-IX, 2022/W/ING/03-49 2022/W/ING/03-12 grants.

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The influence of oil-derived substances on groundwater in the light of isotopic analyses of carbon, oxygen and sulphur

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This abstract is focused on applying isotopic analysis of carbon, oxygen and sulphur as a tool to asses the influence of, covering the first groundwater system, oil-slick of petroleum hydrocarbons. During mineralization of hydrocarbons, both in aerobic and anaerobic conditions (when SO_4^{2-} is reduced), microorganisms produce CO_2. Thus, an increase of dissolved CO_2 concentration, and in consequence of DIC, in groundwater, may indicate progressing biodegradation of hydrocarbons (Coates et al. 1996, Grishchenkov 2000). On the other hand, the DIC originated from decomposition of hydrocarbons, shows relatively low $^{13}C/^{12}C$ ratios as compared to DIC of natural origin (Bolliger et al. 1999, Conrad et al. 1999). Likewise, when microorganisms utilize the sulphate (the terminal acceptor of electrons), its concentration in groundwater decreases, hence the residual sulphate ion becomes ^{34}S-enriched. Based on the isotopic analyses of sulphur and oxygen in the sulphate ion, the dominating mechanisms of decomposition of hydrocarbons polluting the aquifer in particular zones of the oil-slick were tentatively determined. Traditional methods, based solely on chemical analysis are not sufficient enough to identify particular sources of DIC in groundwater, as well as processes regulating the mineralization of hydrocarbons.

Isotopic and chemical analysis indicated, that the zone with a dominating aerobic process of hydrocarbon decomposition is the northern margin of the oil-slick. This zone is characterized by easier oxygen and sulphate ion supply by groundwater, which is indispensable for hydrocarbon mineralization process. The region with the dominating anaerobic hydrocarbon decomposition process is the central part of the oil-slick, where much higher thickness of the oil product was observed. These zones were determined on the basis of DIC and sulphate ion concentrations, as well as their isotopic composition.

Moreover, seasonal variations within the oil-slick were observed. The mean concentration of DIC in groundwater, varied from 228.90 mg/dm^3 for the winter season to 519.47 mg/dm^3 in the summer season. Likewise, $\delta^{13}C_{DIC}$ variations were also observed: the mean value of $\delta^{13}C_{DIC}$ for the summer season was –16.16‰, and that in the winter season was –19.92‰. The increase of $\delta^{13}C_{DIC}$ values is resulted from hydrocarbon decomposition. It is rather possible that the rate of biodegradation can probably be described by mean of the Rayleigh distillation model. Slight seasonal changes were also observed for $\delta^{34}S$ in the sulphate ion. These differences are probably caused by various intensity of sulphate reduction.

Carbon isotope mass balance allowed calculating the percentage of DIC of anthropogenic origin (from hydrocarbon decomposition) in the groundwater within the oil-slick. During the summer season, when biodegradation of oil-derived substances is the most intense, ca. 50 to 54% DIC in groundwater within the oil-slick originates from microbiological decomposition of hydrocarbons. In the winter season, when biodegradation processes are considerably restricted, the percentage of DIC from hydrocarbon decomposition in the groundwater is about 16-31%. Zones with the most intense mineralization of oil-derived substances are areas of the oil-slick with easier oxygen supply (mainly the northern margin). In these areas the content of anthropogenic DIC oscillates from 68 to 72% in the summer season, to 24-33% in the winter season. In the central part of the stain, where anaerobic processes dominates, the content of DIC from the decomposition of oil-derived substances is much lower, in the summer season reaches 41-50%, and in the winter season from 9 to 15%.

This research indicates that isotopic analysis of carbon, oxygen and sulphur consist a useful tool for the quantitative evaluation of the hydrocarbon mineralization.

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Isotopic composition of carbonates from Precambrian apatite-carbonate rocks

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Apatite deposits are found in carbonate and carbonate-silicate rocks which are widespread in metamorphic complexes of the Precambrian areas (Aldan Shield , Peri-Baikal region, North Chinese Platform, Ukrainian Shield, etc.). The rocks comprise a number of morphogenetic types, including primary sedimentary (stratiform and lenticular bodies) and various later rocks (younger carbonate veins and pockets), whose geneses are related to metamorphic and metasomatic processes. The stratiform and lenticular carbonate rocks can be classified into the following groups according to their mineral assemblages: (a) marbles (>95% carbonates), (b) calc-silicate rocks (10 - 75% silicates), and (c) apatite--carbonate rocks (ores).

There are now extensive materials on the isotopic compositions of carbonates from metamorphic and metasomatic rocks. It was established that an increase in the grades of metamorphic and metasomatic alterations is associated with the enrichment of carbonates in light carbon and oxygen isotopes, and the most significant shifts in C and O isotopes from those of the initial sedimentary rocks result in values similar to those typical of skarns and carbonatites. This opens the possibilities of using isotopic data to assay the extent of transformations of the primary rocks.

The isotopic composition of carbon and oxygen was determined in samples of carbonates from rocks of all morphogenetic types of the Aldan and Ukrainian Shields , Peri-Baikal region, North Chinese Platform, etc. Results of carbon and oxygen isotope work performed on different deposits confirm that each of these deposits represents a clearly defined and isotopically distinct sedimentary facies. The values of C and O isotopes for the marbles, calc-silicate rocks, and apatite--carbonate rocks reflect their primary values and are close to those in sedimentary Precambrian carbonate rocks elsewhere. Among the rocks examined, the highest C and O isotopes values were obtained for the apatite-carbonate rocks, whose protolith was produced chemogenically, most probably in shallow evaporitic basins, in a significantly reducing environment, at a limited influx of terrigenous material. The subsequent transformations of the primary rocks by meteoric waters and metasomatic fluids can be identified using low values of O and C isotopes.

The amount of apatite in the protolith was determined by the phosphorus concentration in solutions of the primary sedimentation basins and the fractions of clastic apatite, which was produced by intraformation erosion and weathering of nearby apatite-bearing rocks.

A new type electromagnet controller for isotope ratio mass-spectrometer (IRMS)

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The fundamental advantage of an electromagnet in comparison to a permanent magnet is that the magnetic field can be continuously controlled, including its switch off and reversal of its polarity, by varying of the coil current. The reversal of the magnetic polarity is important when both positive and negative ions spectra have to be investigated as it is the case of positive and negative TIMS. The scanning of mass spectra by varying the magnetic field leads to lower isotope fractionation in the ion source than by varying the high voltage (ion acceleration electric field). This is because that in the last mode low mass ions are extracted more efficiently by a higher voltage than high mass ions.

However use of the electromagnets requires a rather high power supply because the coils are fed continuously from a dc controller. Moreover, such controllers have a limited range of the current regulation. These drawbacks result from the use of transistors at which a voltage excess has to be reduced. In order to extend the range of current regulation, a common dc controller frequently has a switch for a rough matching of the voltage in the power supply, but even with such a switch it is hard to reduce the coil current close to zero and to record a spectrum over a large range.

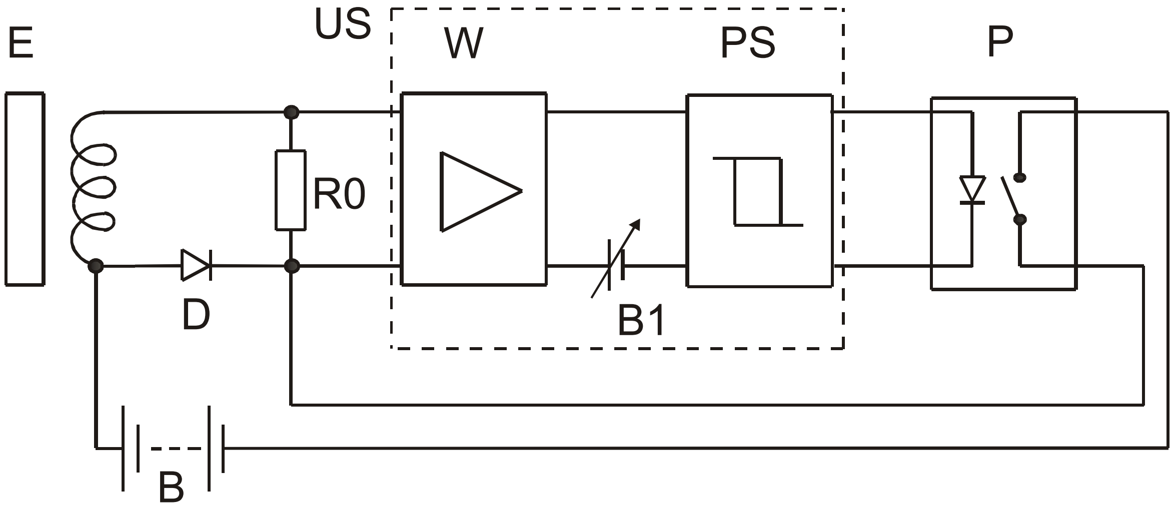

Fig. 1. Block diagram of the switching controller of an electromagnet.

We report here on a novel controller for electromagnets, which is free of drawbacks mentioned above. The power consumed by the switching controller is low, because it is predominantly used for a slight periodic supply of the coil current which is induced just after the controller was switched on. Inasmuch as a typical electromagnet coil has a low coefficient of dissipation energy due to high inductance and low resistance, the power needed for the periodic supply of the coil current is small. A precise adjustment of the coil current is can be made in a continuous manner by setting of the width of the current pulses. That width can be adjusted by means of precise potentiometer (voltage divider) or by a computer controlled reference voltage.

The only drawback – typical for all switching controllers – is a little modulation of the coil current around a very well kept average value (Soclof, 1985). The output ripple factor may be reduced, however, to such a low level that it may be considered as negligible.

A simplified circuit diagram of our switching controller (Halas, Nowak, 2004) is shown in Fig. 1. At the beginning the switch P is ON an the electromagnet coil is fed from a dc source B, the diode D does not conduct. When the coil current is sufficient to produce the desired strength of the magnetic field, the switch P is set OFF, thereafter diode D starts to conduct. In this way the coil current is continued until it drops (due to energy dissipation by all the resistances in the loop comprising the coil, diode D and reference resistor R0) to a designed level. The voltage drop on R0 is amplified and compared with a regulated reference voltage from the source B1. The block PS stands for the Schmitt trigger (a comparator with a hysteresis). It alters the switch P from ON to OFF when the coil current attains desired level, and *vice versa* – from OFF to ON, when the current drops to the value determined by the hysteresis of the Schmitt trigger (Soclof, 1985).

The described switching controller we successfully use in magnetically scanned mass spectrometer for isotope analysis.

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Deuterium Isotope Effect on the Molar Volume of Aqueous Solutions of 3-methylpyridine

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3-methylpyridine dissolved in heavy water exhibits a closed immiscibility loop between 38.5 and 117 °C at normal pressure, while it is completely miscible with water at any concentration and temperature (see e.g. Pápai and Jancsó, 2000, Almásy et al., 2002). The purpose of the present investigation is to compare the volumetric characteristics of dilute solutions of 3-methylpyridine in H_2O and D_2O. Densities of dilute solutions of 3-methylpiridine in water and heavy water were measured over the concentration range of 0.4 - 4 mole% as a function of temperature between 25 and 45 °C using a vibrating tube densitometer. The excess molar volumes for mixtures containing D_2O were found to be more negative than those with H_2O.

From the densities of the mixtures the partial molar volume of the solute at infinite dilution and the coefficients in the virial expansion of the excess molar volume ($V^e = V_{xx}m^2 + V_{xxx}m^3 + \ldots$) in terms of the aquamolality (m, which is the number of moles of solute per 55.508 mol solvent) have been evaluated. The values of the partial molar volume at infinite dilution were found to be slightly higher (about 0.3%) for the solutions in H_2O than for those in D_2O. The temperature dependence of the excess volume second virial coefficient (V_{xx}) representing the contribution of solute pairs to the excess molar volume shows a characteristic difference between normal and heavy water solutions: while the V_{xx}-t curve for H_2O solution is linear in the temperature range investigated, that for D_2O solution shows a maximum at about 35 °C. The solvent isotope effects are discussed in terms of solute-solvent and solute-solute interactions.

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The origin of S and O isotope ratios in lakewater sulphate

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Introduction

Sulphur is an important bioelement and the main form of sulphur in water is the dissolved sulphate. The dissolved sulphate, in turn, is the major substrate for microbial sequestration of organic compounds and inhibitor of methane ebullitive flux from freshwater sediments. This paper reports systematic study of sulphate ion dissolved in water and bubble methane from sediments of 30 freshwater aquifers (lakes, ponds, rivers) from Poland.

Results

The highest concentration of sulphate has been detected in rivers (85.47 SO_4^{2-} mg/l) and in an artificial lake (70.3 SO_4^{2-} mg/l) located in the E margin of the extremely SO_4^{2-}-polluted region, in SW Poland, called Black Triangle (Jedrysek 2000). The lowest concentration of sulphate has been detected in dystrophic and mountain lakes (from 0.5 to about 3.0 SO_4^{2-} mg/l). The lowest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values have been detected in unpolluted lakes in Eastern Poland (-0.94 and 1.38 ‰, respectively). The highest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values have been detected in polluted lakes in western Poland and dystrophic lakes (12.95 16.15 ‰, respectively).

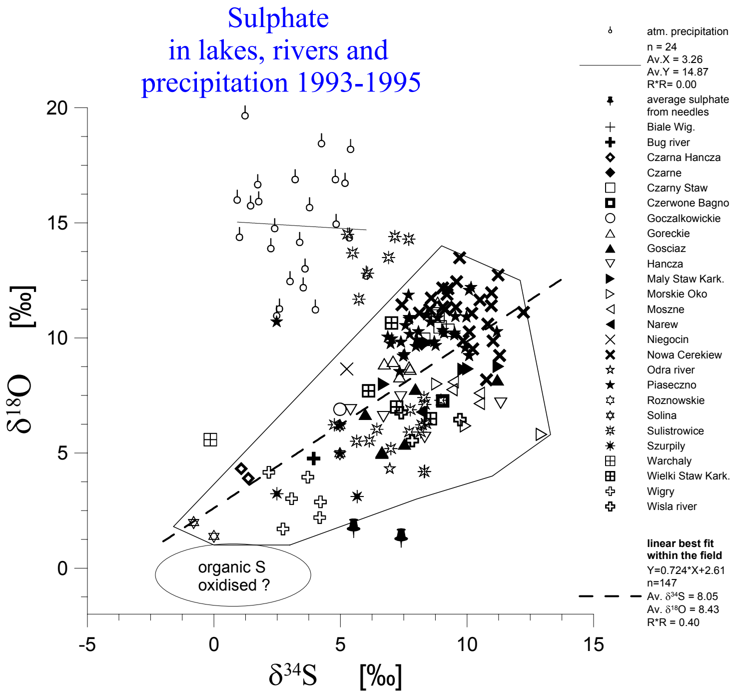

Fig. 1. Sulphur and oxygen isotope ratios in sulphate dissolved in lake water. Sulphur and oxygen isotope variations in lake water may results from some ongoing processes. The points behind the field represents rain from Wroclaw downtown (SW Poland, see Jedrysek 2000), surficial lakewater collected during/after heavy rains or spruce needles sulphate.

Discussion

In the region under study, the anthropogenic sulphate has about 10 ‰ higher $\delta^{18}O$ value than its natural analogue (Jedrysek 2000). The isotopic composition of sulphate in the rain in Wroclaw downtown shows no correlation in the oxygen and sulphur isotope system and the R^2 coefficient is 0.00 (Fig. 2). Therefore, the R^2 = 0.4 found in lakewater sulphate cannot be ignored and should be elucidated.

The isotope signature of sulphate dissolved in lakewater can isotopically evolve due to microbial reduction, mixing with its natural analogues (geogenic, oceanic) or formation of sulphate (oxidation). Therefore, the mixing ratio of these three main sources of sulphate together with reduction of sulphate are the main factors controlling concentration and isotopic signature of the sulphate in lakes. The lake-born sulphate in lakes (aquatic sulphate) is the sulphate formed form oxidation of reduced sulphur compounds in lakes. In contrast to clean lakes, an increase of the $\delta^{13}C(CH_4)$ value with increasing depth of the water column in strongly SO_4^{2-} contaminated lake has been observed (Jedrysek 1998). It may resulted from exceeding of the biological buffering potential of the lake reflected by an active oxidation of methane and methane precursors.

Two biogenic sources of sulphate in lakes, (i) allochtonous or terrestrial that formed by terrestrial organisms (macrophytes, oxidation in soil *etc.*) and (ii) autochtonous aquatic -

that formed by aquatic organisms (*e.g.* Krouse *et al.,* 1991). The $\delta^{18}O$ value of the atmospheric oxygen is rather stable and isotopically heavy, but $\delta^{18}O(H_2O)$ value in precipitation varies seasonally. Likewise, evaporation from lakes causes a significant enrichment of the lakewater, while lakes at higher elevations or at higher latitudes shows lower $\delta^{18}O(H_2O)$ value accordingly to decreasing $\delta^{18}O(H_2O)$ value in meteoric precipitation (*e.g.* Różański *et al.,* 1993). In fact, it has been shown that in precipitation annual variations in the $\delta^{18}O(SO_4^{2-})$ value roughly corresponds to the annual variations in $\delta^{18}O(H_2O)$ (*e.g.* Lloyd 1968; Longinelli and Cortecci 1970; Trembaczowski 1991, 1994).

Lakes are often surrounded by coniferous forests which, in much larger rates than deciduous trees, assimilate SO_2 from the atmosphere and store it in their needles in the form of organic sulphur compounds and sulphate. The sulphate in needles is usually about 3.5 ‰ enriched in ^{34}S isotope compared to organic sulphur. Moreover, in SO_2-contaminated regions, conifers remove excessive sulphur in the form of H_2S, which results in additional ^{34}S and ^{18}O enrichment of the retained needle sulphate (Jedrysek *et al.,* 2002). Sulphate from shedded needles is easy mobilized by rainwater and transported through streamwater and groundwater to the neighbouring lakes. Consequently, the lakes receive additional input of sulphate from coniferous forested catchments. Besides, evaporation of lakes also slightly increases concentration of sulphate, however this is probably less important than the terrestrial biosphere input. In fact, in most mountainous lakes, surrounded dominantly by dwarf mountain pine (*Pinis mughus*) and spruce (*Picea abies*), concentration of the sulphate in lakewater was found to be higher than in the local precipitation (Jedrysek – in preparation). This can be explained from rough calculations. Namely, average concentration of sulphate on the surface of needles, inside needles and organic sulphur is 0.03, 0.01 and 0.1%, respectively (Jedrysek *et al.,* 2002). On the other hand, the total quantity of the litter from coniferous vegetation amounts from about 0.8 to 3.0 t/ha/year (*e.g.* Schall 1991; Oleksyn – oral information) and the total quantity of the litter from, the comparable to the mountain lakes studied, shrub *Pinus mugo Turra* high mountain and subalpine belt of the Romanian Carpathians (1500-2200 m) amounts to 2.6 t/ha/year (Coldea and Plamada 1978). When 20 % of organic S is oxidised to sulphate and when practically all sulphate is removed from shedded needles, the total output of SO_4^{2-} from these needles to the ecosystem is more than 1 t/ha/year. That means that in a typical mountainous lake (small watershed, deep) surrounded by coniferous vegetation, the total input of SO_4^{2-} can be estimated to vary between 10 to 100 mg/l of lakewater per year. Hence, the

SO_4^{2-} is dominantly of allochtonous biogenic origin and from isotopic mass balance point of view the SO_4^{2-} from precipitation is negligible, because concentration of SO_4^{2-} in precipitation is usually between much less than 1 and not higher than 10 mg/l. Consequently, coniferous areas may determine concentration of sulphate in freshwater systems (including groundwaters) thus control oxidation of organic compounds in freshwater sediments and the water column in freshwater systems.

Although, sulphur isotope ratios in the needles (sulphate and organic sulphur) are generally similar to that in precipitation, the $\delta^{18}O(SO_4^{2-})$ value in needles is significantly lower than that in precipitation (Fig. 2). This is due to the fact, and in contrast to atmospheric sulphate (see above), that the needle sulphate forms within the needles and the oxygen in it comes from isotopically depleted water (in average $\delta^{18}O$ during vegetation season is about –12 ‰). In addition, the low $\delta^{18}O(SO_4^{2-})$ value in needles is due to the fact that a large part of sulphate is formed in needles during winter when the assimilation is active and local precipitation show lowest values in the annual cycle. Likewise, it can be expected that sulphate, formed due to oxidation of shedded needles organic sulphur, may show slightly lower $\delta^{18}O(SO_4^{2-})$ value than the needle sulphate when the latter experience advanced reduction resulting in ^{34}S and ^{18}O isotope enrichment of the residual sulphate. Therefore, the allochtnonus sulphate can be largely responsible for the $\delta^{34}S(SO_4^{2-})$-$\delta^{18}O(SO_4^{2-})$ correlation in lakes.

Conclusions

1. Most lakes shows an individual $\delta^{34}S$ and $\delta^{18}O$ signal and relatively little variations in its $\delta^{34}S$ and $\delta^{18}O$ system
2. $\delta^{18}O(SO_4^{2-})$ and $\delta^{34}S(SO_4^{2-})$ values, in many of the lakes, is controlled by mixing ratio between sulphate from precipitation and that of biogenic (allo- and autochtonous) origin and microbial reduction of sulphate. Biogenic sulphate of terrestrial origin can be the main source of sulphate on lakes with watershed dominated by coniferous vegetation.
3. Degraded eutrophic lakes show high $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2})$ values while clean or oligotrophic lakes show low $\delta^{34}S(SO_4^{2})$ and $\delta^{18}O(SO_4^{2})$ values.

Acknowledgments

This study was supported from the State Com.Sci.Res, University of Wroclaw S and W grants, and IAI.

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The Ludfordian carbon isotope excursion in the Vidukle core, Lithuania, its relations with the Lau Oceanic Event and environmental background in NW Baltica

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Five to six notable positive carbon isotope excursions have been ascertained in the Silurian (Kaljo et al., 1998, Munnecke et al., 2003). The most prominent one is widely observed in the upper Ludlow (Ludfordian) of Baltica, Laurentia, Perunica and Australia, indicating true global dimension of this stable isotope event. Due to its stratigraphical position, the excursion has been connected with the Lau Oceanic Event established by Jeppsson (1998) based on different environmental processes and conodont biodiversity changes. Extraordinarily high carbon isotope values (11.2‰ in Scania; Wigforss-Lange, 1999) and serious biodiversity changes in several groups of biota (corals, graptolites, vertebrates, conodonts and acritarchs; see references in Kaljo et al., 1998) occurring approximately in the same interval of the Ludfordian make the event really intriguing. A detailed study of relationships between these two processes and their environmental background is needed to find out real reasons for both the isotope and biotic changes.

A continuous section (320 m) of terrigenous-carbonate rocks of the Wenlock and Ludlow was studied in the Vidukle core in central Lithuania. A total of 113 whole rock samples were analysed. The rock content of the rather deep shelf section shows a general upward shallowing trend interrupted by two relative deepening episodes of the sea in the earliest and latest Ludlow. The Wenlock comprises the Riga Formation (Fm) (claystones with graptolites) and the Siesartis Fm (graptolitic mudstones, limestone interbeds); the Ludlow includes the Dubysa Fm (mainly mudstones with graptolites, higher more calcareous and shelly fauna), the Mituva Fm (limestones, oncolites) and the Ventspils Fm (limestones, silty marls).

The carbon isotope trend shows the following main tendencies and excursions:

1. In the upper part of the Riga Fm the $\delta^{13}C$ values remain below or close to 0‰. In the Siesartis Fm twice slightly higher values were registered: 1.3‰ at 1299.5 m and 1.6‰ at 1284.4 m. Paškevičius et al. (1994) recorded from these levels graptolites, which allow us to date these weak shifts as the *Monograptus ludensis* Biozone. This is a more exact dating than that suggested by Kaljo et al. (1998).
2. The Dubysa Fm shows also low values – in the lower beds below 0‰, but higher, maximum values reach 0.7‰. In the top a negative shift until –1.5‰ (at 1178 m) was recorded. The shift is dated by the last occurrences of *Bohemograptus bohemicus tenuis* and the appearance of *Polygnathoides siluricus* (Paškevičius et al. 1994).
3. In the Mituva Fm the carbon isotope trend changes completely, values of the positive $\delta^{13}C$ excursion reach 8.2‰ (at 1147 m) and beginning from 1178 m (see item 2), the whole shift is 9.7‰. The excursion (values over 2‰) occupies nearly the entire formation (1159–1120 m). A negative shift (–1.2‰) similar to that at the start of the excursion occurs at the boundary with the Ventspils Fm. The excursion is dated based on the last occurrences of *Polygnathoides siluricus* just below the main shift and the appearance of *Ozarkodina wimani* and *O.* aff. *crispa* in the upper part of the excursion (Paškevičius et al., 1994). The true *O. crispa* appears above the negative shift at 1100 m. The conodont occurrences allow us to identify the excursion as the middle Ludfordian.
4. The carbon isotope trend above the last excursion and negative shift returned to ca 1‰ values in the uppermost Ludlow and lowermost Pridoli.

CaO, MgO and the terrigenous component (t.c.) show the following distribution pattern in the Ludlow part of the Vidukle core: (1) The t.c. of the rocks is dominating over the carbonates – clearly in the Dubysa Fm, but slightly in the Mituva Fm. The CaO content is variable but increasing up to the top of the Mituva Fm, where a set-back (down to 21%) occurs. The MgO content is low and varies mainly below 5%, changing parallel to t.c. (2) The $\delta^{13}C$ positive shift coincides with beds where the CaO + MgO content is stably over 40%; both negative shifts occur in the rocks with a high clay content.

Based on the data from the Vidukle core, the following conclusions can be made:

1. The Wenlock carbon isotope excursions are in good accordance with earlier data from Baltica and elsewhere, and the $\delta^{13}C$ values partly reflect the depth of the sedimentary basin.
2. The peak values of the Ludfordian excursion occur in the limits of the Lau Event defined by conodonts, but the rising and falling limbs are at least in part located before and

after the Event, i.e. the processes that caused the carbon isotope excursion started before the Lau Event.

3. The positive excursion began and ended with negative shifts, which are well correlated with certain sedimentological changes, thus evidencing oceanic and climatic processes characteristic of more humid episodes; the positive excursion itself could be referred to an arid episode. The carbon isotope pattern seems to be typical of the event.

4. The environmental change was rather rapid – its implication in terms of the rise in $\delta^{13}C$ values through 30 m was 0.3‰ per metre or 1‰ per 70 000 years, but the last 4‰ were added only in 54 000 years.

The study was partly supported by Estonian Science Foundation (grant 5042).

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An estimation of isotope mass balance of biogeochemical sulphur cycle in forest regions

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Introduction

Sulphur is one of the main element in the biosphere and transformations of sulphur in the nature shows cycling character where variations in red-ox is crucial factor of isotope effects observed.

The biospheric part of S cycling is poorly understood and air pollutions may complicate the picture (Jędrysek *et al.*, 2002). Therefore, spruce needles (*Picea abies*) at the area of Lower Silesia (SW Poland) was selected for our investigations. The SW part of Lower Silesia is called "Black Triangle”. Although considerable decrease in pollution (about 87% for dust and 74% for SO_2) between 1990-2000 has been noted, this region is still under anthropogenic SO_2 and dust impact (WIOŚ, 2002).

Trees assimilate sulphur from two sources: 1) sulphate dissolved in water 2) atmospheric SO_2 (Jensen 1963, Chukhrov et al., 1975, Carlson and Forrest, 1982, Mayer et al., 1995). The sulphur assimilated is turned to three sulphuric amino acids: cysteine, cystin (formated from oxygenation of cysteine) and methionine. Under natural condition, main portion of the assimilated sulphur comes from sulphate uptake through roots (Krouse et al., 1991). Under SO_2 anthropogenic impact, assimilated sulphur comes from atmospheric SO_2 (Rennenberg 1984) and coniferous (especially spruce) show tendency to uptake every quantity of accessible sulphur (Turner and Lambert, 1980).

Under strong anthropogenic impact, assimilation of high amount of sulphur may be balanced by sulphur H_2S emission from plants. This process is controlled by following environmental conditions: concentration of SO_2, light intensity, humidity and age of needles (DeCormis 1968, Wilson et al., 1978, Hällgren and Fredriksson, 1982, Rennenberg 1984, Kałużny 2002, Jędrysek et al., 2002). Under humid conditions (fog, precipitation) H_2S may be easily dissolved and oxidised to SO_4^{2-} (Jędrysek et al., 2002) but some portion of isotopicely light H_2S is emitted to the atmosphere.

Results and Discussion

Concentrations of SO_4^{2-} in spruce needles analysed varied out from 0,0001 to 0,0646 wt.%, with average value about 0,014 %. This values are typical for conifers (Turner et al., 1977, Manninen et al., 1997). Also concentration of organic sulphur (average value about 0,1 %) are comparable to data obtained by other authors (Krouse et al., 1991, Staniaszek 1992, Gebauer et al., 1994, Giesemann et al., 1995).

The $\delta^{34}S(SO_4^{2-})$ value varied from 4,19 to 11,9 ‰ (average about 8 ‰). Correlation of isotopic composition with altitude are noticed: higher $\delta^{34}S(SO_4^{2-})$ value corresponds to higher altitudes. Generally, isotopic data of sulphate in spruce needles show smaller variations as compared to sulphate in precipitation in neighbouring areas (Grescheova *et al.,* 1998, Jędrysek 2000).

Isotopic composition of organic sulphur varied out from 0,03 to 9,16 ‰. It clear correlates with altitude and show relatively small $\delta^{34}S$(S-org) value variations as compared to $\delta^{34}S(SO_4^{2-})$ value (Fig. 1). The difference between $\delta^{34}S$ value of sulphate and organic sulphur ($\Delta^{34}S(SO_4^{2-}$-S-org)) varied from -1,12 to 7,57 ‰, with average 3,70 ‰.

The oxidation state of sulphur is the main factor controlling isotope fractionation in the atmosphere-biosphere-pedosphere system. S^{2-} -bearing compounds are depleted in ^{34}S as compared to S^0 or SO_4^{2-} -bearing compounds (Chukhrov et al., 1975, Toran and Harris 1989). Both $\delta^{34}S$(S-org) and $\delta^{34}S(SO_4^{2-})$ value increase with altitude (Fig. 1). Plants preferentially assimilate ^{32}S isotope, thus the residual sulphur is ^{34}S enriched. Therefore, the higher $\delta^{34}S(SO_4^{2-})$ value of higher altitudes could be explained by on increasing uptake of SO_2 from the atmosphere and consequently increasing emission of H_2S. Consequently, the residual SO_4^{2-} in needles become ^{34}S enriched (Fig. 2).

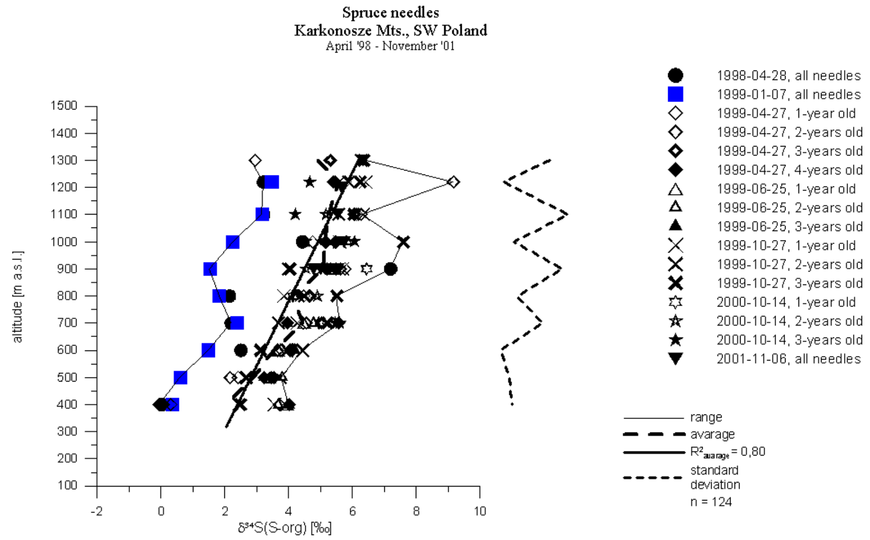

Fig. 1. Isotopic composition of organic sulphur in spruce needles (Karkonosze Mts.).

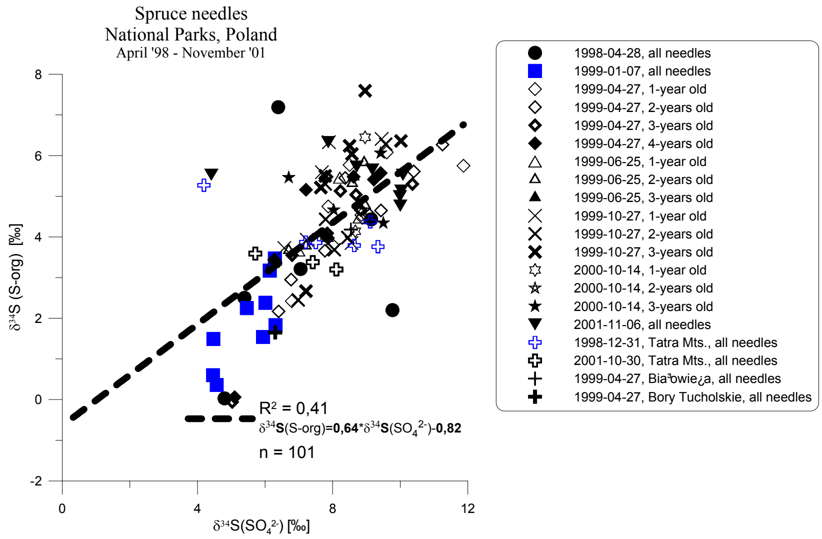

Fig. 2. Isotopic ratio of organic and inorganic sulphur in spruce needles (Karkonosze Mts.).

Isotope mass balance (SO_4^{2-} -H_2S-SO_2 system)

The difference in sulphur isotopic composition of SO_4^{2-} and H_2S under isotope equilibrium ($\Delta^{34}S(SO_4^{2-} - H_2S)$), at temperature 25°C is -63,36 ‰ (Robinson 1973). Likewise, the $\Delta^{34}S(SO_4^{2-} - SO_2)$, at temperature 25°C, is -12,41 ‰ (Sakai 1968). At lower temperatures larger differences of isotopic composition at this systems are expected. Thus, the difference in $\delta^{34}S$ value in SO_4^{2-} -H_2S system should be about 70 ‰. The average difference of isotopic composition of inorganic and organic sulphur ($\Delta^{34}S$ (SO_4^{2-}-S-org) is 3,70 ‰. This evidence isotopic disequilibrium or open S-system. Any change in intensity of H_2S emission should be isotopically detectionable (at precision of isotopic analysis about

0,1 ‰). Therefore, isotopic study in the atmosphere seasonal and diurnal variations of SO_2 and H_2O would allow to describe individual factors controlling emission of hydrogen sulphide and to calculate an isotopic mass balance of H_2S emitted and amount of sulphur stored (in the form of SO_4^{2-}) by forest complexes.

Conclusions

1. Higher value $\delta^{34}S(SO_4^{2-})$ and $\delta^{34}S$(S-org) with higher altitude result from an intensive assimilation SO_2 from atmosphere from the plant and probably growing emission H_2S to atmosphere.
2. Plants can not prevent to uptake of any portion of sulphur in the form of SO_2 through stomata. After assimilation SO_2 is oxidised and accumulate in the form of sulphate in spruce needles.
3. Coniferous forests can be a significant source of H_2S to the atmosphere.
4. Coniferous forests may play significant role in purification of the atmosphere from SO_2.

Acknowledgements

This study was supported by: 2022/W/ING/03, 1017/S/ING/03-IX grants.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Using environmental isotopes to estimate recharge area of the Zagreb aquifer

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The Zagreb aquifer is the most important source of water supply of the town Zagreb, where from about 5,5 m^3/s of groundwater is pumped. It is a part of hydrogeological system situated within the Sava basin and it is made of Quaternary sediments – Pleistocene and Holocene gravel-sand sediments with the prevailing limestone and dolomite pebbles and grains and silt-clay interbeds. Groundwater samples have been taken in various hydrological conditions at 15 piezometric wells at various depths (Fig. 1).

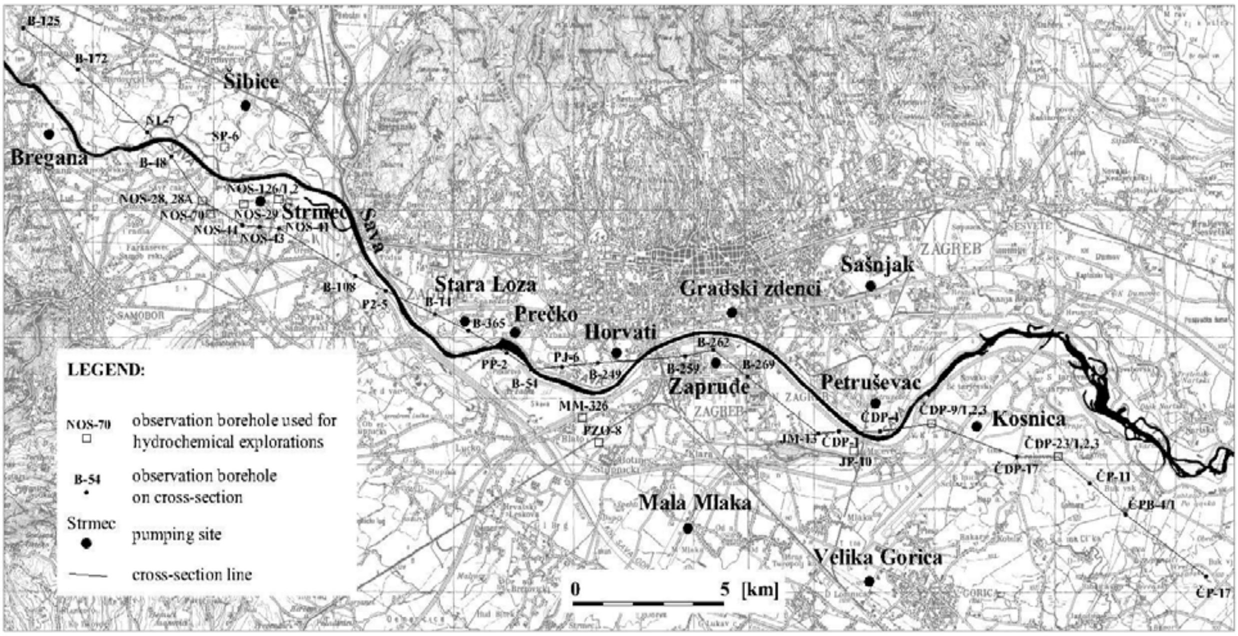

Fig. 1 The position map of piezometric wells

Main ions, stabile isotope of oxygen ($\delta^{18}O$) and hydrogen (δ^2H), radioactive isotope of carbon (^{14}C) and tritium (^3H) were analysed in water samples. According to chemical composition, the groundwater belongs to CaMg-HCO_3 and CaNaMg-HCO_3 to CaMgNa-HCO_3 type (deeper parts of the aquifer in the Strmec area). The increase amount of sodium in the Strmac area is because of hydrolysis of alumosilicates in clayey silt deposits. The groundwater temperature varies from 10 to 16°C. In the shallow parts of the aquifer were observed seasonally temperature changes and in deeper parts of the aquifer temperature changes were slow. Conductivity varies between 400 to 1000 µS/cm, and greater values than this have been measured at the individual piezometric wells downstream from groundwater pollutant. Groundwater from Zagreb aquifer is, according to pH values, slightly acid, neutral to slightly basic. Ratio of δ^{2}H and δ^{18}O indicate that the upper part of the Zagreb aquifer is under influence of water from lower altitude and warmer Holocene climate, but the deeper parts of the aquifer are under influence of regional flow (colder climate and a little bit higher altitude). Measured values on piezometric well JP-10 are like one in the Sava River and values on piezometric well CDP-9 (the Črnkovec area) are more positive, but measured values on piezometric well CDP-23 (the Črnkovec area) are negative and that indicate the influence of the regional flow (Fig. 2). Also, in the deeper parts of piezometric well PP-18 (the Pertuševec area), measured values of δ^{2}H and δ^{18}O are similar to one from piezometric well CDP-23. Measured values of δ^{2}H and δ^{18}O in samples of piezometric well NOS-28 indicate the recharge of that part of the aquifer in the colder period. The activity of tritium and ^{14}C are decreasing on locations CDP-23 and NOS-28 with the depth but their activity is reverse on the location CDP-9 (lower ^{14}C activity in the upper part and higher in the deeper part). Activity distribution of ^{14}C and ^{3}H along the aquifer depth on CDP-23 and CDP-9 locations shows that the whole quantity of water is the result of present recharge, so in its prevailing part, it is the result of precipitation infiltration in the last 50 years (IAEA, 1983, UNESCO/IAEA, 2001). Also, the lower part of the aquifer on the location NOS-28 is under the present recharge but in the deeper part of the aquifer the water is old (typical example of slow water exchange).

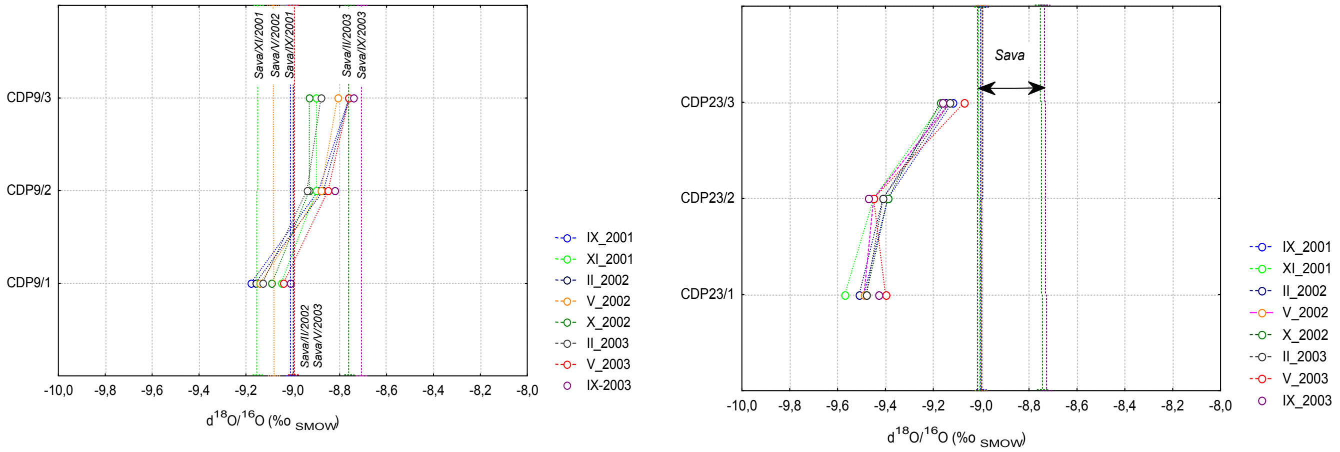

Fig. 2 The distribution of δ^{18}O on locations CDP-9 and CDP-23 along the depth

The Zagreb aquifer in the hydrochemic and isotopic sense is layered, especially in parts, which are far away from the Sava River. The shallow parts of the aquifer are under the present recharge and water in the deep parts of the aquifer has long residence time. Also, the deep parts of the aquifer in the Črnkovec and Petruševec area, which are situated at the opposite side of the Sava River, are unique hydrogeological system.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Stable isotope geochemical and petrographic studies on travertines from Tata, Porhanyó-Quarry (Hungary)

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In the area of the Tata town (Hungary) there are several Quaternary travertine outcrops of which the Porhanyó-Quarry is the best exploited one. The former archaeological studies of the Porhanyó-Quarry resulted in the reconstruction of the Middle Paleolithic Mousterian culture of the site. The principal goal of this work is to define the depositional environment of the Tata travertine by studying the petrographical and microfacies features and stable carbon and oxygen isotope compositions.

The 15 m thick lacustrine travertine can be divided to six units. Unit 1 (14.7-12.4 m) consists of massive, thick bedded, phytoclastic travertine with some gastropods, and covered by a sharp discontinuity surface, parallel to the bedding. Unit 2 (12.4-11.8 m) comprises the archaeological „culture layer" and is build up by a palaesoil horizon at the bottom and siliciclastic fluvial channel deposits at the top. Both are rich in bones, in Palaeolithic human tools, artefacts and show fragments of charcoal. A new discontinuity surface separates the bedded phytoclastic and gastropods bearing travertines of the Unit 3 (11.8-4.5 m) from the „culture layer" (paleosoil layer). 20 to 250 cm wide, from SW to NE directed and mainly open fissures cut the rocks of Units 1, 2 and 3. Some of these fissures represent minor spring vents and cones, filled by vertically and upward conical laminated travertines. The lower boundary of the soft, laminated, phytoclastic travertine of Unit 4 (4.5-2.5 m) is formed by a new discontinuity surface, which covers the vents and cones. Top of Unit 4 is covered by the loose clastic travertine bearing horizon of Unit 5 (2.5-1.0 m), which is imbedded in fluvial-eolian sand. Eolian sand of Unit 6 (1.0-0.0 m) terminates the section.

Eighteen samples were collected from one vertical section for paleoclimatological evaluation. Besides we sampled the most typical carbonate vent as well the other carbonate like forms. Eight samples were taken from one undetermined form which can be either carbonate vent or cascade. At the same time samples were collected from Kőpite-Hill (carbonate cone?) travertine occurence which situated north from Tata town. Petroghraphic and microfacies analyses of on thinsections were performed combined with stable carbon and oxygen isotope measurements. Detailed XRD studies were conducted on bulk samples and on insoluble residue collected in the vertical section and on samples collected from the palaeosoil horizon. Paleomagnetic measurements of the vertical sections were also used to determine the timing of travertine formation.

Algal and other phytoclastic grainstone, boundstone and floatstone are considered dominant microfacies types of travertines. Among the bioclasts fragments of gastropods, ostracods and charas may occur. Travertines are composed mainly of pure, magnesium-free calcite, with traces of dolomite. Low proportion of siliciclastic insoluble residue of Units 1-4 (0,53 %) increases upward unto 2,29 % in Unit 5. Quartz, feldspar and few muscovite represent the scare extraclasts.

The depositional environment was a shallow (1-3 m), plant-dominated lake, dissected by spring cones and vents, which are indicators of the ancient spring activity. These vents appear on the wall of the quarry and NE from the quarry, next to the Öreg-lake. The lake, fed by thermal springs formed in a siliciclastic floodplain or delta system. The springs bought quartz grains with the thermal water from the Pannon siliciclastic bedrock to the surface. These grains are reversed in the centre of the carbonate vents.

The three main lacustrine phases of the lake evolution were interrupted at first by a palaeosoil formation and flooding event, followed up by an fluvial-eolian event and finally finished by eolian sedimentation. The lacustrine phases represent intensive spring activity generating relatively high water levels, while the fluvial to eolian phases are to be connected to reducted spring activity with waterlevel-drops.

Based on the stable isotope investigations the values of the samples taken from the carbonate vents (δ^{13}C (-5,34)-(-5,57 ‰) and δ^{18}O (-12,31)-(-12,87 ‰) differ from the mean isotope values of samples (δ^{13}C= - 5,43 ‰, δ^{18}O = -11,40 ‰) collected from the vertical section and from samples collected from cascades (δ^{13}C (-4,9)-(-5,5 ‰) and δ^{18}O (-10,6)-(-12 ‰) relative to V-PDB. Because of the former intensive spring activity, many carbonate vent were preserved in the quarry. Among the flow path of the water outgassing and evaporation controlled the stable isotope compositions of travertines precipitated. The different facies (vent, cascade, pond) migrated during the evolution of the travertine complex due to changes in morphology and flow direction. Thus, it is not possible to use a simple vertical section to conduct paleoclimatological evaluation on the base of stable isotope measurements. However, distinct isotope compositions characterize the vent and cascade facies that can be used to study the evolution of the complex.

The Tata travertine complex ($\delta^{13}C_{mean}$= -5,3 ‰) show marked $\delta^{13}C$ difference from the travertine occurrences of the Buda Mts. (Buda-Vár-hegy: $\delta^{13}C_{mean}$= 1,5 ‰; Budakalász: $\delta^{13}C_{mean}$= 2,0 ‰), while the stable oxygen isotope compositions are the very similar. Although other processes like upwelling of mantle-derived or metamorphic CO_2 may also produce $\delta^{13}C$ changes, these are shown to be regionally occurring in the Carpathian-Pannonian Region, and thus, the large $\delta^{13}C$ variations at close localities (within about 50 km) are rather attributed to local effects. Presumably the ascending solutions from which the Tata travertine deposited infiltrated through bedrocks rich in organic matter and could have carried dissolved C enriched in light (^{12}C) stable carbon isotope.

Depositional facies and stable isotope geochemistry of some Hungarian travertine occurrences

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Stable isotope analyses on travertines has been started in the last few years in Hungary. Petrographic and geochemical studies were carried out on four different travertine deposits. These occurences have different origins and consequently they revealed diverse isotopic composition (Fig. 1). In addition, the sedimentological processes that influenced the depositional environment and the developed alternating facies can also be followed by the $\delta^{13}C$ and $\delta^{18}O$ variations. We have compared the stable isotope compositions of travertines of different ages (from Cretaceous to recent) and localities (from the Transdanubian Mts., Central Hungary, to the Bükk Mts., NE-Hungary).

The major goal of this study is the analyses of the recent travertine accumulation near Egerszalók (Bükk Mts.). The „Hungarian Pamukkale" located in a small area but represent almost all travertine microfacies type and offers a good opportunity to study stable carbon and oxygen isotope fractionations between water and calcite at surficial conditions.

The water discharges on the slope of a hill and flows down along the slope until it reaches a small basin. We sampled the thermal water and associated travertine accumulations at two different flowpaths and from different microfacies types. The Egerszalók travertine has mean isotope compositions at $\delta^{13}C$=3.1‰ and $\delta^{18}O$=12.1‰. We observed a rapid degassing of CO_2 revealed by the abrupt increase of the carbon isotope values from the vent to the rims (Fig. 2), that is also indicated by the changes of pH values of the water. The measured oxygen isotope values suggest that the cooling of the water has obvious effect. However, our results differ from the theoretical calcite-water isotope equilibrium at the given temperatures (Fig. 3).

The Tata travertine complex ($\delta^{13}C_{mean}$= -5.3 ‰) show marked $\delta^{13}C$ difference from the travertine occurrences of the Buda Mts. (Buda-Vár-hegy: $\delta^{13}C_{mean}$= 1.5 ‰; Budakalász: $\delta^{13}C_{mean}$= 2.0 ‰), while the stable oxygen isotope compositions are the very similar.

The Pleistocene travertine complexes (Tata, Kőpite Hill, Budakalász, Buda-Várhegy) show small δ^{18}O scatter, but their δ^{13}C ranges show marked differences. The δ^{13}C variations may be related to local effect of organic matter oxidation (see Kele et al., this volume). The Buda-Várhegy occurrence has δ^{18}O values similar to the Egerszalók deposit known to be formed at elevated temperature (up to 60 ºC), thus the locality-related δ^{18}O changes may be related to formation temperature differences. The Tata complex was studied in detail that indicated significant differences in the vent and cascade facies. The stable isotope compositions – as well as its origin - of the presumed upper Cretacous travertine cone of the Vértes Mts. differ completely from those of the younger travertine occurrences (Siklósy et al., this volume). However, the within-complex variations are rather similar in the travertines with marked differences between different depositional facies. The δ^{13}C-δ^{18}O correlations and shifts can be modelled by cooling, degassing and disequilibrium calcite precipitation using the analogue of the recent carbonate formation.

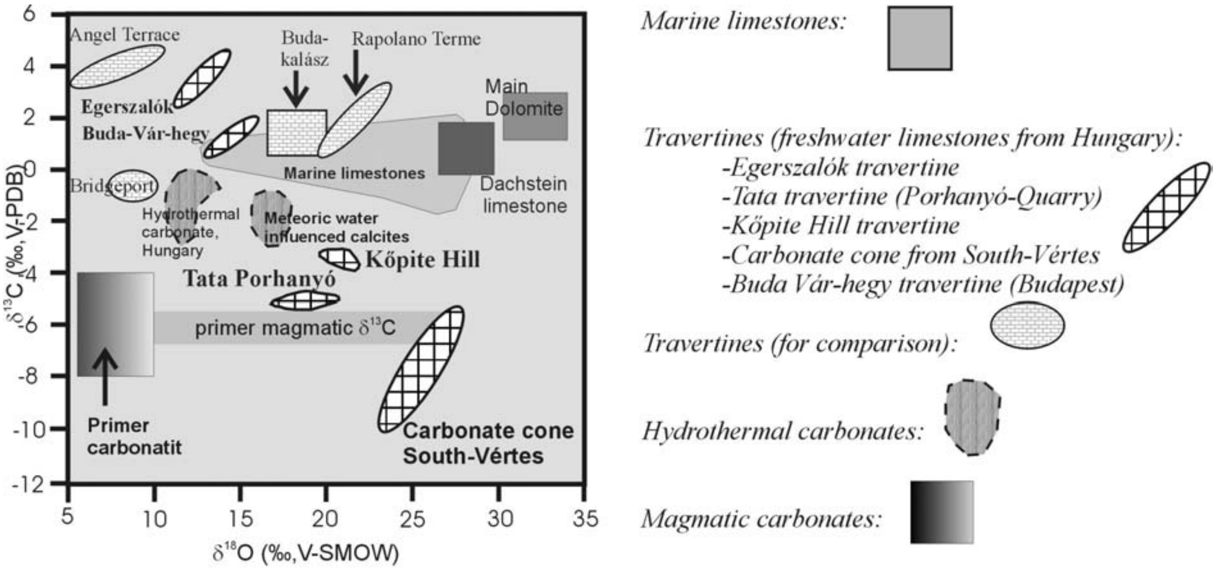

Fig. 1. Stable carbon and oxygen isotope values of different originated carbonates.

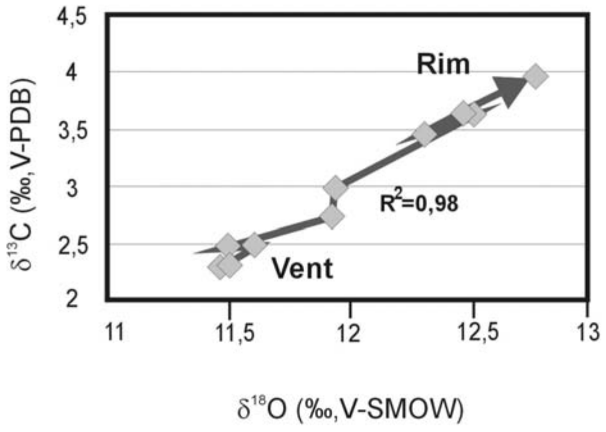

Fig. 2. Isotopic composition of the Egerszalók travertine. Samples were collected along the flow direction.

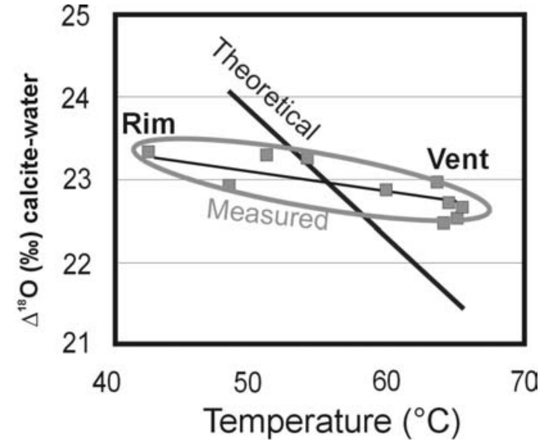

Fig. 3. The theoretical and measured oxygen isotope fractionation between the calcite and water

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Geochemical and isotopic composition of historical mortar and plaster in Styria, Austria

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Historical buildings are constructed of geo-materials, mortar, and plaster of various compositions. Mortar and plaster are man-made materials. Thus, the chemical and isotopic composition comprises information about the historical environment with respect to the provenance of the materials, processing, and specific applications. Moreover, isotopic data may provide additional information about the ancient composition of carbon dioxide and water. The present study is focused on the mineralogical, chemical and isotopic composition of dated and well-characterized carbonate mortar and plaster of roman, medieval, and early modern (pre-industrial) times in Styria (Austria).

Mortars and plasters were sampled from historical buildings in the area of Flavia Solva, Frauenberg, Deutschlandsberg, Seggauberg, Kleinstübing, Niederhofen, Södingberg, and Graz. Sampling was conducted from the exterior to interior mortar layer, wherever applicable. The sampled materials mostly consist of a $CaCO_3$ (calcite) cement with aggregates of quartz and additional silicates like clay minerals. The analyzed Sr/Ca and $^{87}Sr/^{86}Sr$ ratios of the cement are between 0.00030 and 0.0023, and 0.7093 and 0.7104, respectively. These ratios reflect the composition of the natural deposits used for manufacturing of lime mortar. The respective values depend on the environment of formation and on the mineralogical composition (e.g. calcite or aragonite) of the primary limestone.

However, the distribution of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in the carbonate mortars and plasters indicates a more complicated situation as isotopic compositions comprise a wide range of $\delta^{13}C_{CaCO3}$(PDB) from -24.2 to -0.8, and of $\delta^{18}O_{CaCO3}$(PDB) from -23.9 to -2.6$^{o}/_{oo}$. The stable carbon and oxygen isotope distributions in the carbonate cement displays an almost linear correlation. In general calcite is continuously isotopically “heavier” from the exterior to the interior mortar layer. The range and systematic correlation of the data reflect isotopic fractionation effects upon setting of the cement and during the history of the individual cement.

In principle isotope distributions depend on the composition of the gaseous CO_2 and aqueous OH^- according to the overall reaction:

$$Ca(OH)_2 + CO_{2(gas)} \rightarrow CaCO_3 + H_2O \quad (1)$$

during the formation of carbonate cement. Reaction 1 is accompanied by a kinetic isotope fractionation due to the hydroxylation of gaseous CO_2 (Dietzel, 2000), resulting in an enrichment of ^{12}C versus ^{13}C in the precipitated $CaCO_3$. If gaseous CO_2 is delivered from the present Earth`s atmosphere ($\delta^{13}C_{CO2(atm)}$ = -7 $^{o}/_{oo}$) a $\delta^{13}C_{CaCO3}$ value of about -25$^{o}/_{oo}$ is obtained. Evolution of oxygen isotopes is more complex and yield $\delta^{18}O_{CaCO3}$ values of about -20 $^{o}/_{oo}$ for calcite precipitated according to reaction 1 (Dietzel et al., 1992). Upon setting of the cement, the diffusion of gaseous CO_2 and subsequent reaction to $CaCO_3$ leads to a continuous enrichment of ^{13}C and ^{18}O (versus ^{12}C and ^{16}O, respectively) of CO_2 within the gas phase along the cement setting path. Accordingly, precipitated calcite is isotopically “lighter” at the exterior mortar layer.

The results show that analyses of carbon and oxygen isotopic compositions permit to follow the historic cementation process, and to detect potential variations of the composition of the atmospheric CO_2 and liquid (H_2O). Variations may be caused by natural or anthropogenic impacts, e.g. evaporation of H_2O and burning of coal, respectively. From another point of view, secondary processes like interaction with isotopically “light” soil-CO_2 or re-crystallization of carbonate cements in the presence of H_2O from various origins may be deciphered.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

Tritium and stable isotope variations in precipitation of Croatia and Slovenia

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Monitoring of isotope composition (^{2}H, ^{3}H, ^{18}O) of monthly precipitation at Zagreb (Croatia, 157 m a.s.l.) and Ljubljana (Slovenia, 299 m a.s.l.) has been performed since 1976 and 1980, respectively (Krajcar Bronić et al., 1998) within the Global Network for Isotopes in Precipitation (GNIP) organized jointly by the Isotope Hydrology Section of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). The GNIP network includes also monitoring of meteorological data (amount of precipitation, mean air temperature, mean atmospheric water vapour pressure) on monthly basis (IAEA, 2004). The type of climate at the two stations is continental, with yearly amount of precipitation of 883 mm (yearly mean for 30-year period) and 1394 mm, and mean yearly temperature 11.4°C and 9.8°C, in Zagreb and Ljubljana, respectively.

Within the IAEA Co-ordinated Research Program "Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate" the network has been extended to several stations along the Adriatic coasts of Croatia and Slovenia in the period between September 2000 and December 2003: Portorož-Airport (2 m a.s.l., 13.1°C, 911 mm) and Kozina (497 m a.s.l., 1511 mm) in Slovenia, and in Croatia Malinska on Krk Island (1 m a.s.l., 14.8°C, 1306 mm), Zadar (5 m a.s.l., 15.9°C, 937 mm), Komiža on Vis Island (6 m a.s.l., 17.6°C, 706 mm), Dubrovnik (52 m a.s.l., 17.2°C, 1092 mm), and Zavižan on Mt. Velebit (1594 m a.s.l, 4.3°C, 2113 mm/year). The sampling sites are characterized by different types of climate (continental and Mediterranean, or mixing influence) and the corresponding mean monthly temperatures and mean yearly precipitation amounts for the same period are given above in parentheses. The lowest mean temperature and highest amount of precipitation were recorded at Zavižan. Marine stations at southern Adriatic show higher mean temperatures than the continental stations, while at the North Adriatic mean temperature lies between the continental and marine values.

Long-term tritium records for stations Zagreb and Ljubljana show that in the past mean yearly tritium activity concentration in precipitation continuously decreased after reaching a global atmospheric maximum in 1963 due to thermonuclear bomb-tests in mid-20th century (Krajcar Bronić et al., 1998). The observed seasonal variations are typical for the continental stations of the Northern Hemisphere with winter minima approaching in the last years the natural pre-bomb tritium level (≤0.4 Bq/L). Maxima are observed in early summer, and reach presently up to 2.1 Bq/L. The seasonal variations in the last decade were less pronounced than in the period 1976 – 1990. Thus, mean yearly tritium concentrations in Zagreb and Ljubljana precipitation during the last decade are ~1.1 Bq/L.

Tritium activity distribution at the north Adriatic coast is similar to that at the continental stations, showing just slightly lower mean values. Seasonal variations at maritime stations of mid-Adriatic and especially of south-Adriatic are less pronounced (summer maxima reach 1.4 Bq/L) and the mean yearly activities are lower than those at the continental and north-Adriatic stations due to sea-water evaporation influence - mean tritium activities in precipitation in Zadar, Komiža and Dubrovnik are equal to 0.75 Bq/L, 0.70 Bq/L and 0.46 Bq/L, respectively. Tritium distribution pattern and the mean tritium concentration at Zavižan (0.78 Bq/L) are closer to those of the Mediterranean stations in the vicinity than to those of the continental stations. Tritium activity concentrations in monthly precipitation at all three stations in Slovenia vary seasonally from ≤0.4 to 2.2 Bq/L and are typical for the continental stations of Northern Hemisphere.

The stable isotope composition of precipitation shows different patterns of seasonal variations at continental and maritime stations. The continental stations show larger seasonal variations in the stable isotope content (*e.g.*, seasonal variations equal to ~13‰ in $\delta^{18}O$ at stations Zagreb and Ljubljana), compared with the maritime stations (*e.g.*, 11.6‰ and 8‰ at stations Komiža and Dubrovnik, respectively) due to larger temperature differences in summer and winter. At the high-altitude station Zavižan on Mt. Velebit the two types of climate, the Mediterranean and the cold continental one, are mixing. The isotope pattern of precipitation reflects such a mixing: tritium distribution is close to the nearest maritime station Zadar, while the seasonal variations in stable isotopes are close to the continental pattern (seasonal variations in $\delta^{18}O$ equal to 13.7‰).

Correlation of $\delta^{18}O$ with mean monthly temperature is good for all stations. The long-term (1976-2001) slope of the correlation line for Zagreb is 0.3‰ $\delta^{18}O$ per °C. Similar values are obtained for north- and mid-Adriatic stations, while for the south-Adriatic stations the slope is 0.15‰ $\delta^{18}O$ per °C. For the coldest Zavižan station the slope is 0.4‰ $\delta^{18}O$ per °C.

The correlation between $\delta^{18}O$ and $\delta^{2}H$ is very good for each station and obtained data fit well to the “Global Meteoric Water Line”, $\delta^{2}H = 8\ \delta^{18}O + 10$. Some deviations were observed in summer months and are probably a result of partial evaporation of raindrops. However, a detailed inspection shows that the slope is higher (close to 8) for the continental stations and Zavižan, while the maritime stations have smaller slope (about 7). The mean values of deuterium excess ($d = \delta^{2}H - 8\ \delta^{18}O$) are also different: 13 for Zavižan, ~7.5 for Zagreb and Ljubljana, and between 7 and 9 for mid- and south-Adriatic stations. Higher monthly values of *d*-excess (above 12) were also occasionally observed and can be attributed to precipitation from the Mediterranean Sea.

As the station differ in their altitudes, it is possible to estimate the so-called altitude effect for the region. For the continental stations the decrease of 0.37‰ $\delta^{18}O$ per 100 m altitude difference is obtained, while for the stations in the coastal region (including Zavižan) the decrease is 0.26‰ $\delta^{18}O$ per 100 m altitude difference.

The presented data shows present-day temporal and spatial distribution of tritium and stable isotopes ^{2}H and ^{18}O in precipitation of a relatively small area rich in climatic diversity. The data can be used in various applications, such as climatology and hydrology.

Acknowledgement The work performed under the IAEA Research Contracts RC11265 and RC11267, the Project 0098014 by the Ministry of Science, Republic of Croatia, and the project of bilateral co-operation "Isotopes in precipitation" between Croatia and Slovenia.

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Contributions from stable light isotopes to understanding the dietary ecology of early hominins in southern Africa

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Determination of carbon and oxygen isotope values from tooth enamel to obtain information about the dietary ecology and environments of Pleistocene, Pliocene and even Miocene fauna has by now become widely applied. As one example, a significant body of isotopic data now exists for South African hominins and associated fauna during the Plio-Pleistocene allowing us to make robust deductions about their dietary ecology. The data show that, almost without exception, hominins interacted with grassy environments independently of environmental shifts, which were significant over this time. Their diets were weighted towards carbon from C_3 (woody plants, shrubs and herbs) sources but show significant C_4 (tropical grass) contributions which demonstrate either direct consumption of grasses or C_4 sedges, or indirect consumption of grass-eating animals (both vertebrates and invertebrates), or both. Termite 'hunting' has been independently suggested from examination of bone tool wear at Swartkrans but carbon isotopes alone do not permit trophic distinctions. Relatively low oxygen isotope values for all hominins in comparison to associated fauna show similarities with suids, certain monkeys, and faunivores. These patterns are as yet poorly understood but some promising subtle distinctions are emerging from studies of modern assemblages, such as between insectivores and carnivores. On present evidence consistent hominid interaction with grassland foods, at whatever trophic level, seems deeply rooted even before significant brain expansion with emergence of early Homo, setting both Australopithecines and the genus Homo firmly apart from chimpanzees in their dietary ecology.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Comparison of different stable hydrogen isotope-ratio measurement techniques for tracer studies with deuterated water in the unsaturated zone and in groundwater.

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Stable isotopes of the water molecule have proved to be extremely useful tracers in the unsaturated zone and in groundwater. However, the use of the natural fluctuations of these isotopes as tracer signal is often limited, because the variations in isotope ratios are too small or (and) the input function is unknown. In such cases the application of isotopically enriched water as tracer could be very useful. Water enriched with the isotopes ^{18}O, ^{3}H and Deuterium have been used by several scientists around the world to describe ground-water flow (Gaspar, 1987). We have used deuterated water as a reference tracer several times, mainly in karst aquifers (Benischke et al., 2003) but also in the saturated and unsaturated zone of porous groundwater aquifers. The objective of these experiments was to compare different types of tracers and their behaviour during transport as well as the degree to be classified as conservative or non-conservative. Deuterated water has advantages over ^{18}O-enriched or depleted water, however, in that it has a smaller natural abundance in nature and it is much more affordable. It has the advantage over tritium in being non-radioactive (Becker and Coplen, 2001). Other advantages of deuterium as a groundwater tracer are that it is non toxic and the sampling is very easy. The main disadvantage of the deuterium was for a long time the expensive and time consuming analysis.

With the development of new hydrogen isotope-ratio measurement techniques, it is now possible to measure hydrogen with automated dual-inlet methods or in continuous-flow mode in full automatic way. Examples of stable hydrogen isotope-ratio measurement techniques currently are in use include the equilibration of water with hydrogen gas in the presence of a platinum catalyst (Horita et al., 1989), reduction of water to H_2 using Cr metal in automated dual-inlet (Gehre et al., 1996) or continuous-flow mode (Morrison et al., 2001) and high temperature continuous flow pyrolysis using a carbon based reactor (Begley and Scrimgeour, 1997).

We have used three of these techniques and evaluated the advantages and disadvantages of the different methods for the application of deuterated water in groundwater tracing. The best analytical precision (<1‰) has been achieved with the automated equilibration of water (3mL) with H_2 gas in the presence of a platinum-based catalyst. However, the method is time consuming and not very useful to analyse a big number of samples in a short time. With continuous-flow isotope ratio mass spectrometry using chromium as the reducing agent we were able to measure a sequence of 100 samples per day with good analytical precision (1-2‰). The memory effect was negligible for samples in the natural abundance range of 1.5‰ δD-values. The lowest precision (2-3‰) was obtained by high temperature continuous-flow pyrolysis using a carbon based reactor. In addition, a clear memory effect was observed when waters with very different δD-values were analyzed sequentially. In result of our investigations the on-line continuous-flow reduction of waters with chromium as reactive reactor component has a number of significant advantages over automated equilibration and on-line carbon-based pyrolysis. However, using some modifications of the reactor design, the memory of a carbon based reactor can be reduced to values below 1.5 % (Gehre, 2004).

Comparing deuterium with other groundwater tracers we found that Deuterium and Bromide have showed the highest degree of conservativeness, whereas Na-Fluorescein and moreover Sulphorhodamine G have showed significant retardation as it was expected (Benischke et al., 2003). A direct comparison was difficult due to the different sensitivity of the analytical procedures, because sensitivity of dye tracer analytics as well as Bromide and Deuterium analytics differ from each other over several order of magnitudes. We found that the minimum detectable concentration of deuterium in practice is about 0.1 mg/L above background. Similar values have been reported by Becker and Coplen (2001).

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Sediments of lakes, ponds and floodplains as archives of environmental changes using ^{210}Pb

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Sediments from lakes, ponds and rivers record events caused by man and by natural processes and, by using radioactive tracers, their timing can be determined (W. R. Shell, 1982). ^{210}Pb method has been widely used for dating of lacustrine and marine deposits, peats and glacier ice. Recently this method has been used for riverine overbank sediments (Walling & He, 1999). The use of ^{210}Pb method allows for retrospective (for last 100-150 years) estimates of sedimentation rates. This paper presents attempts to use this technique to estimate rates of sediment deposition in various environments: the Pisia and the Swider rivers (central Poland), Morskie Oko and Zelene Pleso lakes (Tatra Mountains) and a pond in the Ruda river valley (Upper Silesia, Poland). Rivers selected for the study fulfil the requirement of regular flooding in the studied reaches what is a prerequisite for estimations of overbank sedimentation rates by use of ^{210}Pb (He & Walling, 1996a).

Rates of overbank sedimentation on floodplains and their spatial variability significantly influence suspended solids budget in a catchment and long-term evolution of the floodplain (Walling, 1999). Due to importance of overbank sediments in the assessment of the anthropogenic environmental change there in an increasing need for information regarding rates and spatial patterns of overbank deposition. The Pisia and the Swider are small lowland rivers characterized by different flood regimes and rates of overbank sedimentation. Catchments of both rivers underwent significant anthropogenic changes over last 150 years reflected, among others, in varying sedimentation rates, sediment compositions and metal contents.

High mountain lakes trap unconsolidated slope covers which are subject to downslope transfer due to mass movements and fluvial transport. Sediment transfer changes spatially and temporally depending on slope morphology and covers and the degree of its stabilization by vegetation. Therefore, similar thermal and precipitation regimes result in different sedimentary responses for lakes located in two postglacial valleys. Results from the Morskie Oko and the Zelene Pleso lakes illustrate this difference. Sediment rates derived by use of the ^{210}Pb method are 0.037 and 0.044 cm/year, respectively. (Baumgart-Kotarba, et al. 1993; Kotarba et al., 2002).

Sediments of the pond in the Ruda river valley represent a specific sedimentation environment. The artificial pond was operational in the second half of the XIX century. Its bottom sediments are buried underneath younger fluvial deposits. The ^{210}Pb method was applied to the pond sediments. The average sedimentation rates was estimated at 3.0 g/cm^2 year what corresponds to 0,5 cm/year.

The ^{210}Pb method appeared to be a useful tool in studies of environmental changes as recorded in sediments of different lacustrine and fluvial environments.

Acknowledgements

The presented work was supported by National Grant KBN-11.11.220.01, by KBN statutory founds 10.10.140.038 and financial support from the Kosciuszko Foundation, Inc., American Center for Polish Culture, with funds provided by the Alfred Jurzykowski Foundation.

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Carbon isotopic composition of atmospheric CO_2: contaminated and non-contaminated areas

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CO_2 is one of the primary agents of global climate changes. The increase of atmospheric CO_2 concentrations is essentially related to human-induced emissions and, particularly, to the burning of fossil fuel. Continuous records of CO_2 concentrations were repeatedly carried out along hemispheric courses from Italy to Antarctica by the use of a vessel of the Italian National Research Program in Antarctica. During these expeditions discrete air samples were collected in 4 liter Pyrex flasks in order to carry out precise carbon isotope analyses on atmospheric CO_2 from different areas including theoretically "clean" open ocean areas as well as highly polluted sections. Samples were collected during the 1998-'99 expedition as well as during the 2001-'02 and the 2003-'04 expeditions. The flasks were carefully evacuated to 10^{-3} mmHg , opened on the windward side of the ship 15 meters above sea level and closed after air collection by means of high vacuum greasless stopcocks. The flasks were then stored in wooden boxes kept at room temperature until the arrival of the ship at the final harbour in Italy.

The CO_2 samples were separated from other gases in the laboratory by means of a vacuum line by very slow pumping (about 6 ml/min) through a Swagelock microvalve and a liquid nitrogen cooled spiral trap. After pumping down the flask to about 10^{-3} mmHg the trap was isolated by means of high vacuum stopcocks and heated to about - 80°C by means of an ethyl-alcohol-liquid nitrogen slash. The evolving CO_2 was collected in a sample tube and measured in a Finnigan Delta S mass spectrometer against a standard CO_2 obtained from a very pure Carrara marble, calibrated against NBS-19 and NBS-20 international standards. The standard deviation of the carbon isotope measurements ($\delta^{13}C$), tested on air samples collected with the same procedure and treated in the same way ranges from ± 0.02 to ±0.04 ‰ (1σ).

The data obtained show, as expected, a relatively large atmospheric pollution in the Mediterranean area and particularly in the Adriatic Sea and near the coast of Egypt. In the Mediterranean area South-Westerly winds tend to reduce the effect of atmospheric pollution even though, despite a large variability of CO_2 concentrations, these values are systematically higher (from a few ppmv to about 15 ppmv) than those measured in open ocean "clean" areas.

A marked pollution is apparent in the area of the Bab-el-Mandeb strait where the $\delta^{13}C$ was found more negative (up to about 2 ‰) than in the Southern Red Sea and in the Arabian Sea and Indian Ocean. This effect is likely related to the pollution caused by the oil refineries in the Gibuti area.

The concentration of atmospheric CO_2 over the "clean" Indian Ocean increased from 365 ppmv at the end of 1998 to 372 ppmv at the end of 2001 to 377 ppmv at the end of 2003. Simultaneously, the mean $\delta^{13}C$ value of atmospheric CO_2 over Indian Ocean decreased from -8.07 ‰ at the end of 1998 to -8.17 ‰ at the end of 2001.

The isotopic values of atmospheric CO_2 over the Mediterranean, Red Sea and Indian Ocean at the end of 2003 will be measured soon, the flask samples collected during the last expedition being expected at the Parma laboratory within the end of April.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

The Antarctic Circumpolar Current: occasional or seasonal source of isotopically light CO_2 ?

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Despite the increasing production of human-induced CO_2 emissions, the CO_2 growth rate in the atmosphere is considerably lower than expected. According to recent estimates (Houghton et al., 2001; Sarmiento and Gruber, 2002) during the Eighties the average fossil-fuel emissions were estimated at 5.4±0.3 Petagrams of carbon per year (1 Petagram - Pg - is equal to 10^{15} g and synonymous with one gigaton - Gt - ; the addition of one Pg of carbon to the atmosphere increases the concentration of CO_2 by about 0.47 ppmv). The atmospheric growth rate was 3.3±0.1 PgC/yr, the difference of 2.1±0.3 PgC/yr being taken up by the oceans and land. During the Nineties, the emissions exceeded 6 PgC/yr (Battle et al.,2000) but the increase of the atmospheric burden of CO_2 during the same period was abot 2.8 PgC/yr. The balance of the CO_2 was taken up by the oceans and the land biosphere. The importance of the knowledge of the CO_2 global distribution in space and time and of its yearly growth rate is apparent. Continuous records of the CO_2 concentrations in the ocean atmosphere were carried out repeatedly during the last decade between Italy and Antarctica by means of a Siemens Ultramat 5E analyzer assembled for shipboard use. During the same expeditions discrete air samples were collected in 4 liter Pyrex flasks between New Zealand and Antarctica in order to carry out accurate measurements of the carbon isotope composition of atmospheric CO_2 over the circumpolar oceans and to compare them with the carbon isotope values obtained from the samples collected over the Indian Ocean from Africa to New Zealand.

Considerable differences were found between the samples collected during four expeditions (1998-’99, 2001-’02, 2002-’03 and 2003-’04). During the 1998-’99 expedition all but three of the samples collected exhibited $\delta^{13}C$ values close to -8.1 ‰, this value being almost identical to those measured on Indian Ocean samples. This value can be considered characteristic for that period for “clean’ areas, far away from a direct contribution of polluting emissions from continental areas. The three anomalous samples were collected between about 52°S and 60°S and show $\delta^{13}C$ values ranging from - 8.45 to - 9.59 ‰. The possibility of pollution from the ship engines has been discarded according to several reliable considerations. During the 2001-’02 expedition only two anomalous samples have been measured, both at a lower latitude (about 48°S and 52°S respectively) the $\delta^{13}C$ values being -11.2 and -10.5 ‰. During the 2002-’03 expedition nine anomalous samples have been measured, located between about 58°S and 67°S the $\delta^{13}C$ values ranging from about -8.7 to about -9.9 ‰ . The flask samples collected during the 2003-’04 expedition are expected at the Parma laboratory within the end of April and will be measured right away.

It should be pointed out that the isotopic changes in the carbon isotopic composition are not paralleled by detectable changes in the atmospheric CO_2 concentration. This involves the rate of the net air-sea CO_2 fluxes with no detectable deviation of fCO_2 from atmospheric equilibrium values. A seasonal variability of the regional CO_2 fluxes has been already recognized in the sub-Antarctic area but the number of anomalous samples collected during the 2002-’03 expedition is quite large to be only the effect of minor seasonal variabilities of regional CO_2 fluxes. The interpretation of these data is complicated by the results obtained by several authors measuring the carbon isotopic composition of DIC. Almost all the results reported are positive while the reported isotopic composition of the anomalous samples is definitely related to very negative CO_2 deriving from the oxydation of organic matter of marine origin. We hope that the samples collected during the last expedition will help to understand the conditions of the air-sea CO_2 fluxes during austral summer in the circum-polar Antarctic area.

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Tracking Fluids, Climate and Crystal Chemistry using the Stable Isotope Compositions of Clays

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The use of stable hydrogen and oxygen isotopic compositions of clay minerals to determine the origin and evolution of pore water in low temperature environments, and to deduce temperatures in these systems, was first elucidated by Sheppard *et al.* (1969), Savin and Epstein (1970) and Lawrence and Taylor (1971, 1972). Today's presentation provides an overview of our group's applications of these principles in sedimentary systems, and outlines some current challenges.

The stable isotopic analysis of secondary minerals in the pore-systems of sedimentary rocks has been a standard technique for elucidating fluid movement and evolution in sedimentary basins since the 1980s. For example, diagenetic clays provided a definitive stable isotopic record of Eocene influx of meteoric water into most sandstones in the northern portion of the Western Interior Basin of North America. This occurred in response to mountain-building during latter stages of the Laramide Orogeny (Longstaffe, 1993). Likewise, H- and O-isotope analyses of secondary chlorite and illite provided evidence for tectonically motivated, multiple episodes of rock-water interaction along the Precambrian-Paleozoic unconformity in the Appalachian Basin of North America (Ziegler and Longstaffe, 2000a,b). Hot basinal brines, driven westward by Taconic orogenic events, controlled chlorite formation. Illitic clays formed later from local meteoric water during basement reactivation related to distal Acadian and Alleghanian orogenic activity. A similar approach was possible in the quite different tectonic setting of the Dead Sea Graben. There, the stable isotopic compositions of secondary minerals provided evidence for multiple (and layered) fluid regimes (Longstaffe et al., 2003). In each case, the understanding of regional paleofluid behaviour provided insight into the distribution of hydrocarbon and mineral deposits.

There have also been practical applications to petroleum exploitation. For example, steam is injected into very viscous deposits of the Alberta oil sands (the largest hydrocarbon accumulations in the world) to facilitate *in situ* hydrocarbon recovery. Steam generation adds considerably to the cost of hydrocarbon extraction. Hence there is interest in understanding its movement in the subsurface, and in particular, whether or not the steam is interacting with the targetted reservoir as planned. Changes in the hydrogen and oxygen isotopic compositions of clay minerals can be used to trace the extent and temperature of contact between the injected fluid and the reservoir.

The climate archive stored in the isotopic compositions of hydrous minerals from ancient soils has been pursued with increasing interest since the mid-1990s. The goal is to understand the nature and rates of fluctuations in Earth’s temperature and humidity, particularly in mid-continental regions. We have examined the hydrogen and oxygen isotopic compositions of pedogenic clay minerals from Cretaceous paleosols from northern regions of the Western Interior Basin. These results have been used as a proxy for paleo-precipitation, whose isotopic composition, in turn, can be used to infer temperature and prevailing atmospheric moisture conditions at that time (Vitali et al., 2002). Holocene climate change in mid-continental North America is of more pressing interest. The complex relationships amongst the oxygen isotopic compositions of grass phytoliths (opal-A) and coexisting cellulose on one hand, and source water, temperature and humidity, on the other hand, are gradually being deciphered (Webb and Longstaffe, 2002, 2003). As a result, grass phytoliths and cellulose have potential as isotopic paleoclimate proxies in ancient soils where both phases accumulate.

The stable isotope approach presumes that hydrous minerals can be isolated and analyzed without changing their original isotopic compositions. We have evaluated most of the common pretreatment methods. We have learned that ‘less is best’. Stable isotopic study of hydrous minerals also depends upon reliable knowledge of mineral-water fractionation factors. Patience is a virtue in measurement of mineral-water fractionation factors at low temperatures. Years of growth, for example, were needed to provide convincing experimental measurements of the O- and H-isotope fractionation factors for gibbsite (Vitali et al., 2001). Post-formational isotopic exchange between hydrous minerals and ambient water is also of concern. Debate still rages concerning the coupled (hydroxyl group) versus decoupled (proton) nature of isotopic exchange between hydrous phases and water.

Different minerals are affected differently, in ways still being discovered. For example, 1.0nm halloysite exhibits significant oxygen (in addition to hydrogen) isotopic exchange at room temperature, a feature largely absent from the 0.7nm variety. A still greater challenge is provided by the possibility that some hydrous minerals inherit part of their compositions from precursors. Experiments involving transformation of berthierine (a 1:1 layer, Fe-rich clay mineral) to saponite (a 2:1 layer smectite) suggest that such inheritance can occur. This observation challenges yet another assumption commonly employed in interpretation of the stable isotopic compositions of clay minerals.

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Isotope Hydrological Study of the Pasnyag Karstic Spring

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The water of the Pasnyag spring of the Aggtelek karst system in Hungary is applied as drinking water. Subsequent upon the local hydrogeological conditions probably in that water fresh and old ground water components are mixed in certain ratio. The objective of this work was to determine the mixing ratio of the waters of different origin. Water sampling was carried out from the spring and a nearby monitoring well.

Helium content and isotope ratio, tritium concentration (by ^{3}He ingrowth method), radiocarbon content of dissolved inorganic carbon (DIC), and δD, δ^{13}C, δ^{18}O isotope ratios were measured from the water samples.

On the basis of isotope measurements the water of the spring and the observed nearby monitoring well are composed of fresh and old components in different ratios. The fresh component is dominant in the Pasnyag spring. The tritium and radiocarbon concentration of this water shows that it is fresh, young water coming directly from the karstic system, with only small amount of DIC from the limestone. The low tritium and radiocarbon content of the F1 monitoring well (nearby the Pasnyag spring) proved that this well contains high amount of old water. The higher helium content and the higher radiogenic ^{4}He ratio of the water also indicate subthermal origin in this case.

3D modelling of isotope ratios in geological bodies

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Introduction

The main goal of this work was to construct a tool for three-dimensional computer modelling, and consequently visualization, of isotopic variations in rock massifs. The method applied is based on computer programming. The real time modelling enable to introduce geochemical parameters (e.g. isotope ratios in rocks and fluids, water-to-rock ratio, temperature, α fractionation factor *etc*.) and observe results directly on the computer display. The "module building" applied (plugging) enables to use the tool in various geological units and larger areas of diverse geological structure.

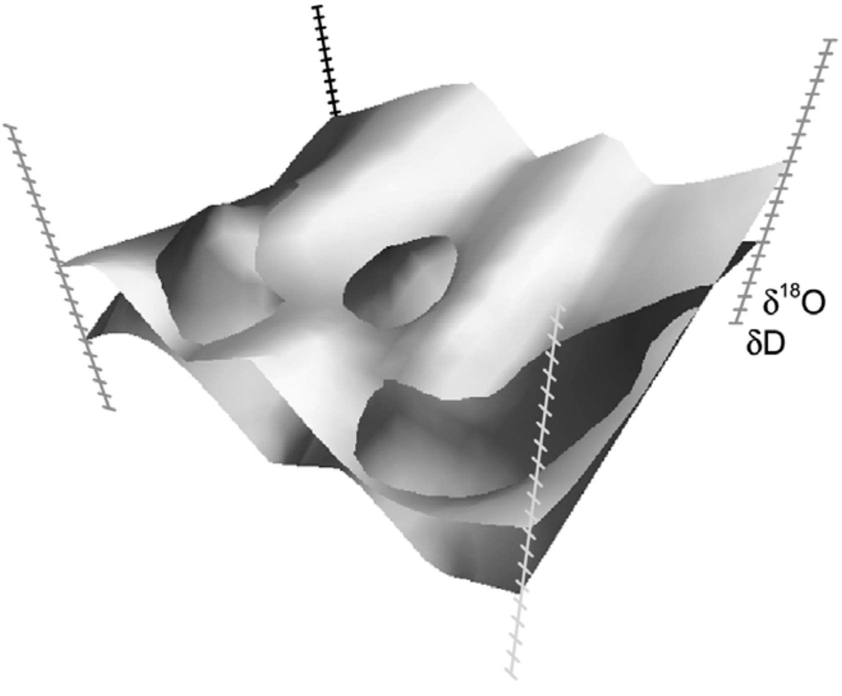


Fig. 1: Computer-generated model of spatial distribution of hydrogen and oxygen isotope ratios

Discussion: The modeling of the isotopic composition of the whole rock

The spatial distribution of isotopic composition of minerals and rocks are interpolated and written in the numeric matrix and these is be represented as a surface. Therefore, isotopic variations of different minerals in a massif can be shown as subsequent surfaces, one above another, which have the same dimensions and position with respect to X-Y-Z axis - spatial variation of isotopic composition of these minerals is observed. This method enable to carry out mathematical calculations with respect to these surfaces, manipulate with them in non-linear way and accept hypothetical values to test the model. Finally, the output is be the outcome matrix of the accepted model.

In practice, we have tested this technique to observe the final isotopic composition of water in ultramafic rocks during serpentinization and while changing, in the real time, the water-to-rock ratio when the Rayleigh distillation model is applied. Obviously, more than one parameter can be modelled or changed the free way, to describe the fluid motion through the rocks. The Fig. 1 shows two crossing surfaces. Four surfaces showing the initial and final isotopic composition of rock and fluid have to be constructed, when calculate spatial distribution of the water-to-rock ratio. When manipulate with one vertical coordinate of any of the surfaces in the selected area, variations in water-to-rock molar ratio can be observed. To discriminate between these surfaces, we have used separate colours for different surfaces and saturation of the respective colour represents the magnitude (value) of the parameter modelled.

Discussion: modeling the isotopic composition of veins

The isotopic composition of veins compared to their spatial orientation may help to find direction of fluid flow and sequence of events (Mydłowski and Jędrysek, 2003b). However, the spatial distribution of isotopic composition of vein-forming minerals requires advanced knowledge with respect to variation in the orientation of veins. Another problem

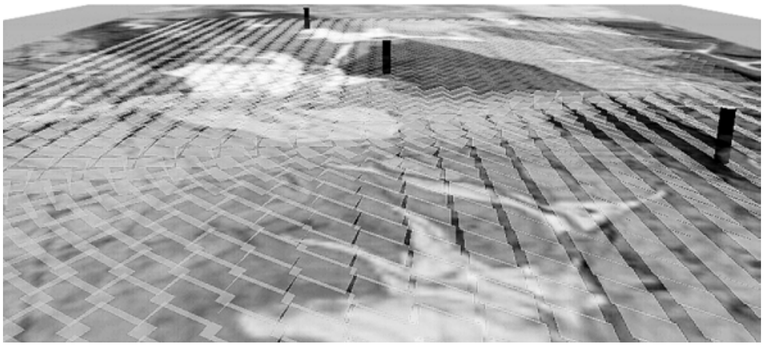
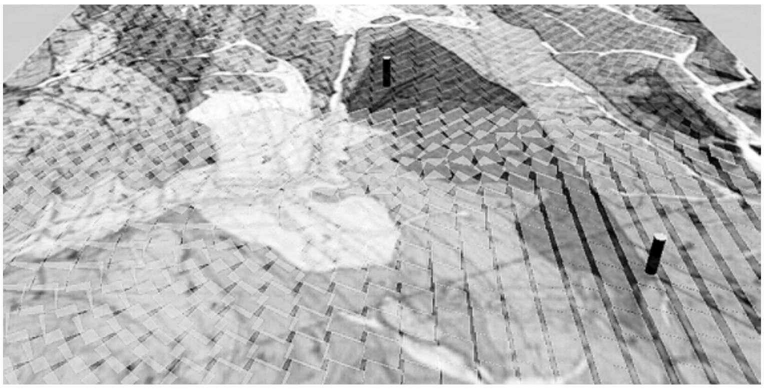


Fig. 2. Spatial distribution of fracutres in Nowa Ruda serpentinite massif (SW Poland) – view 1.

appears when compare isotope ratios of veins to isotopic composition of the host rock Namely, the thickness of veins, especially when the a vein show several meters thickness and is isotopically independent from the host-rock, become important parameter.

It is important to apply the model when large amount of veins occur, because the model become statistically reliable (Mydłowski and Jędrysek, 2003a). The same situation concern fractures. The Fig. 2 and 3 show the orientation of two perpendicular fracture systems in the Nowa Ruda serpentinite massif (SW Poland). This fractures, shown here as a set of surfaces with the same dimensions, can represent fluid flow pathways. When one know the relation between the isotope composition of mineral in the vein and in the rock, some attempts can be made to find spatial distribution of water-to-rock ratio.

Fig. 3. Spatial distribution of fractures in Nowa Ruda serpentinite massif (SW Poland) – view 2.



Conclusions

Numeric modelling of isotopic composition in the real time three dimensional system enable a simple and reliable visualization of fluid flow and water/rock isotope exchange, observe spatial a temporal variation in water-to-rock ratio and temperature, etc. This is very important to describe geological processes especially in the open system.

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The Qaidam basin in Western China: monitoring Himalayan-Tibetan tectonics and climate evolution

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We studied the formation of the unique intracontinental, intermontane Qaidam basin (Western China) in relation to the formation of surrounding Altyn, Kunlun and Qilian mountain belts at the northeastern edge of the Tibetan plateau. This region accommodates in part India-Asia convergence by eastward lateral extrusion and internal shortening of the Qaidam block. The Qaidam basin covers ca. 120,000 square kilometers, and comprises a maximum 16, in average 6 – 8 kilometers thick basin fill. It was initially formed during Paleocene/Eocene, started to subside mainly during early Oligocene, is active at present comprising up to ca. 3,500 meter thick Quaternary sediments, and displays prominent Pliocene to Recent contractional deformation, which resulted in folds and thrusts. The basin floor shows crustal scale folding with a wave length of ca. 30 - 40 kilometers. This suggests an unusually strong rheology of the deeper crust, likely due to predominance of mafic rocks. These relationships suggest the peculiar feature of the Qaidam basin, which must have a much rheologically stronger crust than adjacent mountain ranges.

The surrounding Altyn, Kunlun/Qimantagh and western Qilian mountain belts were deformed and uplifted during the same Eocene/Oligocene to Recent time interval. They include the sinistral Kunlun and Altyn faults which partly accommodate N-S convergence by eastward lateral extrusion. ^{40}Ar/^{39}Ar age dating combined with structural studies give evidence of a major Oligocene ductile shear zones as precursor faults of the present-day Altyn and Kunlun faults, and evidence their significance for the formation of the Qaidam basin.

Because of entirely interior (endorheic) drainage of the Qaidam basin, the volume of denuded mountains largely balances the amount of sediments in the basin. Detailed work on detrital mode of sandstones display exclusively orogenic sources with nearly no variation through time. Only the biotite content increases towards Quaternary monitoring increasing aridity with time. $^{40}Ar/^{39}Ar$ age dating of single, detrital muscovite grains show exclusively late Neoproterozoic, Late Ordovician-Silurian and late Permian/Triassic sources, which can be found in adjacent mountain belts.

The Sr isotopic composition of carbonates does not show any variation through time. Stable oxygen and carbon isotopic compositions of Eocene to Quaternary carbonates monitor regional climate change, mainly increasing aridity and some tectonic events due to the uplift of Tibetan-plateau. Major tectonic steps are during middle Oligocene (ca. 30 Ma), early Miocene (ca. 20-18 Ma), and late Pliocene/early Pliocene. In this later step sharply increasing aridity resulted in deposition of evaporates.

The folded Neogene and Quaternary sediments with its unusual characteristics, e. g. high thickness and tension gashes filled with halite, gypsum or coelestine, allow characterizing the stepwise Pliocene and Quaternary shortening due to transpression and lateral extrusion. Field relationships suggest the following succession of palaeostress orientation tensors, from which D_3 to D_5 are relevant for the final structure of the basin. Normal faults of the D_2 deformation stage are overprinted by N-S and ca. E-W trending strike-slip faults and by NE-trending thrust faults which indicate together NNW-SSW to NW-SE contraction. The overprint of the Qigequan Formation examines the Pleistocene age of deformation. Deformation stage D_4 includes N- and S-dipping thrust faults and WSW-trending sinistral and N- to NNE-trending dextral strike-slip faults suggest ca. N-S to NE-SW contraction. This stage indicates clockwise orientation of the maximum principal stress σ_1 in accordance with results of palaeomagnetic investigations. Deformation stage D_5 is characterized by NE-SW trending dextral and WNW-ESE trending sinistral, in part active strike-slip faults, which argue together ca. E-W contraction. Such faults are common in the western Qaidam basin. A few faults along active E-trending fault traces show Recent stress conditions.

Together, the palaeostress data are characteristic for an extrusional wedge which moves out of the zone of maximum contraction. Clockwise rotation of the principal maximum shortening direction from NW-SE (D_3) over N-S (D_4) to NE-SW to final overall shortening including E-W contraction (D_5) is due increasing inhibition of contraction by resistant forces.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Dating of the Old Bridge in Mostar

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The famous arch bridge (Fig. 1) in Mostar, Bosnia and Herzegovina, was built in 1557-1566 by order of sultan Süleyman the Magnificent. This single-arch stone bridge was constructed by Turkish architect Mimar Hayruddin at the place of an older wooden construction and was 19 m high, with the span of 28.7 m. The bridge was destroyed in war 1993, and has been reconstructed during last several years (Fig. 2). During the reconstruction of the Old Bridge, the remnants of two older bridges were found — a wooden construction that preceded the stony bridge, and an even older wooden suspended bridge. According to documents, mainly from the Dubrovnik Archives, the first suspended bridge crossed the Neretva River by the beginning of the 14th century, while the following wooden bridge was built during the campaign against Turks of the Croato-Hungarian king Matthias Corvinus in 1466, probably by the Ragusian architect Paskoje Miličević.

Eight wood or charcoal samples from various periods of construction of the bridge were dated by the ^{14}C method, and were given for dendrochronological analysis. The oldest beam used in construction of the first pre-Turkish suspended bridge has been dated to 11th century by both methods. Two other beams taken from the uncovered construction of the suspended bridge, as well as two charcoal samples from the basement of the Tara tower on the left bank of the Neretva River, are dated to 14th century. The beam associated with the second wooden bridge is dated to the second half of the 15th century, and the beams connected with the reconstruction of Hayruddin's stony to 18th century. Good agreement between the calibrated ^{14}C and dendrochronological ages is obtained.

Fig. 1. Old Bridge in Mostar

Fig. 2. The bridge under reconstruction

Performance of the Aarhus IsoPrime Mass Spectrometer

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The Aarhus stable isotope ratio mass spectrometer, a GV-Instruments IsoPrime, has been inoperation since August 2002. Stable isotopes ratios of δD ,δ^{13}C and δ^{15}N have routinely been analysed by the continuous flow method, whereas δ^{13}C also has been measured by the classic dual inlet method. This poster demonstrates the performance and quality assurance programme for the Aarhus IsoPrime stable isotope ratio mass spectrometer.

Memory Effects in Continuous Flow Hydrogen Stable Isotope Ratio Analysis on Water Samples

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In this study we focus on methodological refinements of ^{2}H/^{1}H analysis by isotope ratio mass spectrometry. Our experimental setup is a Micromass (now GV-Instruments) IsoPrime coupled to a EuroVector Elemental Analyser Pyrolysis system. We analyse 0.4µL pure water samples at a rate of 200 samples per day with standard deviations on 0.3 to 0.5‰. As described by Morrison *et al* 2001 this system is known to suffer from memory effects of approximately 1% of the intersample δD transition. Stable isotope ratios of deuterium have routinely been analysed at the Aarhus AMS ^{14}C Dating Centre since August 2002. Initially we found memory effects of ~6% which by now has been reduced to 1-2%. A systematic investigation of inlet parameters influencing the memory effect has been carried out in order to find the optimal setting for the smallest possible intersample memory effect. Also the long the term trends such as consumption of reactor chromium and the operational history of the system has been investigated.

The high precision enables improved ice layer counting in ice cores at greater depths. Corrections of raw isotopic data for memory effects are therefore decisive. By our investigation of the intersample memory effect we have designed an analytical model for corrections. We have found the intersample memory effect to be well described by a double exponential function, whereby we are able to split the effect in short and long terms. Longterm effects can reach back as far as 20 samples. This model has successfully been applied to stable hydrogen isotopic data from the GRIP ice core.

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Uranium series dating of the Neanderthal footprint at Vârtop Cave, Romania

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Early human footprints are rare in the fossil record. A survey of the literature reveals only two well documented and dated cases. The first, from ~325 kyr in Italy, represents a very early, pre-Neanderthal human. The other, from ~117 kyr in Africa, is probably a *Homo sapiens* print. Here we report the first clear *Homo neanderthalensis* footprint. It was found in Vârtop Cave, Romania. The individual stepped into calcareous mud that later hardened. The 22 cm long print suggests a body height of ~1.46 m; a gap of 1.6 cm marks the separation of big and second toes. The date of the footprint is constrained by the date of the deposition of the mud (~97 kyr, dated by U-Th isochron method) and the date on the base of a nearby stalagmite on top of the mud (~64 kyr). Thus the Vârtop Cave individual lived in Romania sometime between 97 and 64 kyr, long before the appearance of *Homo sapiens* in Central and Eastern Europe, the earliest records of which date from only ~40-30 kyr. To our knowledge, this is the first recognised and dated *Homo neanderthalensis* footprint.

Isotopic Composition of Precipitation in Hungary in the Last Three Years

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Tritium is one of the most commonly applied environmental isotopes in isotope hydrology. It is suitable for calculation of the age or – more exactly - the mean residence time of very young (<10 years) environmental water. Essential input parameter of models used in these calculations is the distribution of the tritium concentration in the precipitation. The aim of this work was to get a time series of the tritium content of precipitation characteristic for Hungary and to identify those factors, which have essential influence on the changes of tritium content.

The rainfall events are continuously sampled in Debrecen, East-Hungary from December 2000. Tritium, deuterium, and oxygen-18 content of the precipitation samples are measured. We have found that the tritium content of the precipitation changed between 4.8 and 18.0 TU in 2001, between 4.4 and 20.3 TU in 2002, and between 3.5 and 19.8 TU in 2003, with an average of 10.4 ± 0.3 TU, 10.7 ± 0.3 TU and 8.7± 0.3 TU, respectively. The decreasing in the average tritium concentration of precipitation in 2003 was due to the very wet winter, while the year 2001 and 2002 were quite similar.

In addition to the seasonal effect we demonstrate the effect of temperature, meteorological fronts, and cyclones on the tritium content and delta values of precipitation. On the basis of satellite images (© EUMETSAT 2001-2004) and meteorological data we determine trajectories in order to decide which moisture source brings the water vapour.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Radiocarbon dating of some mineral relics of a ship cargo and their carbon isotope geochemistry

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A unique discovery has been made recently at the wreckage of a sunken ship, in the shallow littoral zone on the bottom of the Baltic Sea (Chebowski and Kowalski, 1999). A sand layer 0.5 to 1.7 m thick covers the wreckage of a wooden ship along with elements of the cargo and equipment lying at depths of 5-7 m, ca. 500 m from the shore. The transported cargo included iron plates and bars, and the equipment included barrels filled with wood tar, the organic material used those days for protection of wooden components of ships. The catastrophe leading to the sinking of the ship with equipment and members of the crew according to written sources took place on the Baltic Sea during a storm on the 27th of September 1785. Due to spilling of the wood tar transported in barrels, beneath the wrecked ship, which got stuck in the sandy bottom, a culture layer comprising the sunken iron cargo, ship equipment and bodies of the crew was formed. The physical and chemical conditions at the sea bottom allowed formation of siderite ($FeCO_3$) in such environment.

Samples of siderite and wood tar were collected from the wreckage of a sunken ship, in the shallow littoral zone on the bottom of the Baltic Sea for studies of siderite-water oxygen isotope fractionation in low temperatures and subjected also to radiocarbon determination. Because of small amount of accessible samples of siderite and wood tar, the radiocarbon measurements were performed by accelerator mass spectrometry (AMS) technique. Graphite targets were prepared in the Gliwice Radiocarbon Laboratory and sent for measurements to Kiel, Germany. The radiocarbon dating provided following results: 760±20 BP for siderite and 715±25 BP for wood tar.

The above results were calibrated with use of OxCal programme in order to obtain the calendar age of samples (see Figure 1). Both ages are concordant, indicating the age of samples to ca. 1300 AD, what is unfortunately inconsistent with historical date of sinking (1785 AD). This discrepancy can be explained by incorporation of old carbon, which was present on the ship in form of fossil coal used as a fuel source. Simple calculation allows estimating ca. 7% content of coal of infinite age would be required to produce observed shift of calendar age. Such amount is not unlikely in dated samples, as the present-day rock, which was formed under the isolation of the spilled wood tar includes chips of fossil coal as well as other fragments of the ship equipment and human remains. Nevertheless, the consistent radiocarbon content in both samples supports the geochemical model of the siderite formation established on the basis of stable oxygen and carbon isotopes analysis, which will be published elsewhere (Halas, Chlebowski, 2004)

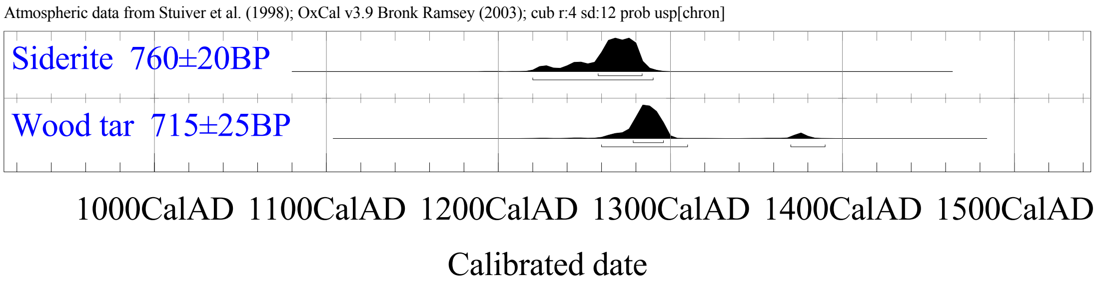

Fig. 1. Calibration of radiocarbon age of investigated samples.

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Role of sulfur isotopes to classify geochemically Pb-Zn mineralisation

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The first attempt to classify geochemically Pb-Zn deposits was made by Schroll et al. (1994). Amongst other geochemical parameters, sulfur isotopes in sulfide and sulfate minerals play an essential role. Sulfur originates: i) from the hydrothermal source produced .by magmatic processes or by fluid-rock reaction or by organic matter; ii) from the reduction of sulfate, originating from coeval seawater or evaporites in the geochemical environment of metal precipitation. Sulfate is not stabile under high temperature condition,. and is reduced by Fe (II), C and organic matter. Sulfate reducing bacteria are responsible for H_2S production, if porosity, moisture and nutrients within the temperature limit (~ < 100°C) are available.

In the high temperature range (~>370°C) H_2S and SO_2 are the mayor components of magmatic gases. The isotope composition is commonly around $\delta^{34}S$ 0‰. Isotopic equilibrium dominates within sulfide minerals ($\delta^{34}S$ FeS_2>ZnS>PbS, Ohmoto & Rye 1974). In hydrothermal deposits <370°C) isotopic equilibrium between sulfide and sulfate is observed > 300°C. Isotopic equilibrium between the sulfide phases $\delta^{34}S$ FeS_2>ZnS>PbS is reported > 150°C (Ohmoto & Rye 1974). Organic matter produces H_2S by decomposition of organic sulfur-compounds or thermochemical reduction of sulfate (TSR). The sulfide sulfur isotopes are heavy ($\delta^{34}S > 0$‰), and the $\delta^{34}S$ difference between sulfide and sulfate is <20 ‰. Bacteriogenic sulphate reduction (BSR) reveals the largest isotope fractionation, i.e. $\delta^{34}S$ values around -100 to +100‰. Bacteriogenic activity is indicated by wide spread of isotope data due to environmental influences and mixing of heavy sulfur from hydrothermal sources. Indications of BSR are macro-, micro- and nano-textures of the ores, oxisulfides, valency states of sulfur, organic compounds etc (Kucha et al 2001). Newly, fossil bacterial bodies were indicated in zinc-ores of Bleiberg (Kucha et al. 2004). However, light sulfur may originate also from the metal-bearing hydrothermal fluids by leaching of sedimentary iron sulfides in the depth or in the environment of the deposit (Ohmoto and Goldhaber 1997). At temperature of > 200°C, isotopically light sulfide sulfur may produced by sulfate reduction in isotopic equilibrium under special conditions.

Sulfur isotopes are useful to characterize low temperature carbonate-hosted Pb-Zn deposits (Schroll and Rantitsch 2003). The precipitation temperatures are commonly lower than 150°C. The temperature range of the oil window (~ 110°C °C) is important for the transition from bacteriogenic sulfate reduction (BSR) to thermochemical reduction (TSR) in deep horizons (Machel 2001). The sulfur isotope characteristics in the three main types, i.e. MVT (Mississippi type), IRT (Irish type) and ATP (Alpine type), is shown in Table 1. MVT-deposits are formed by burial processes, IRT- and APT deposits by pre-burial events. Late mineralisation stages may be influenced by the thermical history.

Multiple sulfur isotopic analysis using a new ion microprobe multicollector technique promises to be an additional mean to identify biological and abiological sulfur fractionation.

Table 1: Sulfur isotope characteristics of MVT -, IRT - and ATP - Pb-Zn deposits.
An attempt considering natural diversity.

	MVT	IRT	APT
Community	Disequilibrium of $\delta^{34}S$ in FeS_2<(PbS, ZnS) and in $\Delta\ \delta^{34}S_{\text{sulfate-sulfide}}$		
$\Delta\ \delta^{34}S_{\text{sulfide to sulfate}}$ (Mostly coeval seawater)	Low (<20‰)	~ 40‰	up to ~ 40‰
Sulfate reduction	TSR	BSR	BSR
Hydrothermal sulfur (Second sulfide sulfur source)	Not present	around 0‰ $\delta^{34}S$	around 0‰ $\delta^{34}S$

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^{14}C, ^{13}C and ^{18}O isotopes in the recent plants of Wigry Lake

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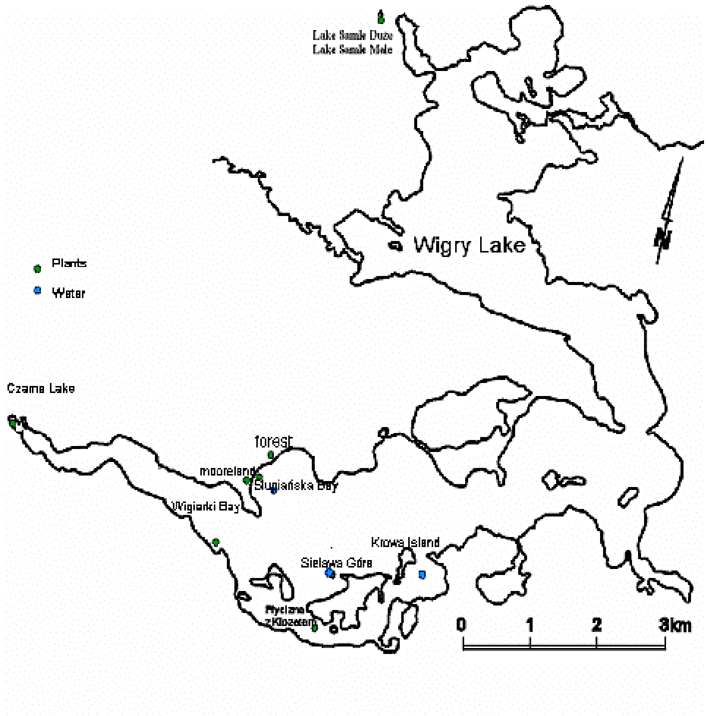
Lake Wigry is located in the north-eastern Poland close to the Polish-Lithuanian border. It belongs to Wigry National Park together with 41 surrounding lakes. The area of Wigry National Park was shaped during Baltic phase of last glaciation and lakes were formed by retreated glacier. Lake Wigry is elongated ribbon lake type, while in the area there are also marginal lakes and thaw lakes.

The Park is dominated by forest communities (16 groups) mainly spruces and pines, alder swamps, swamp forests, as well as marshy meadow and fests growing on dry ground. The most common forest complexes in Wigry National Park are: red grass dry-ground forest, similar to mixed coniferous forests,sub-boreal coniferous pine forest, typical dry-ground forest, covering approximately, different clusters of alder carr and riverside carr.

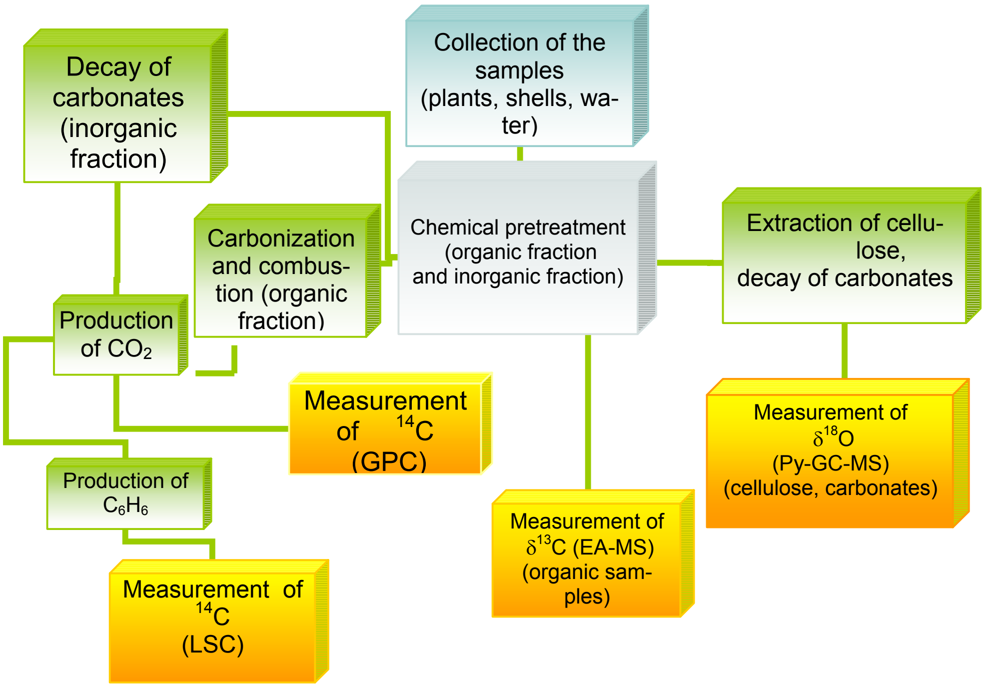
A significant number of vascular plant species present in the Wigry National Park is associated with the aquatic environment and wetlands. Their existence depends on the diversity and quality of lakes, rivers, water-heads, wet meadows, moors and wet forests. The natural plant communities are concentrated on lowmoors, transient moors and high moors located throughout the area of the Park.

The natural carbon mainly consist of three isotopes: ^{12}C, ^{13}C and ^{14}C. The radiocarbon oxidized to carbon dioxide, mixed with the inactive atmospheric carbon dioxide enters the bio- and hydrosphere. To know more about the carbon cycle in contemporary sedimentation environment of Wigry Lake, the samples of plants (Scots pine, Sorediate Tube Lichen, Peat moss, Common Reed, Yellow Pond, Bulrush, Lesser Pond-sedge, Water soldier, Hornwort, Perfoliate Pondweed and Muskgrass- make up, Perfoliate Pondweed, Muskgrass, Eurasian water-milfoil, Sedge, Moss, Willow Moss, Unidentified make up), shells and water were collected from lake and its environment (aquatic, wetland and woodland areas) on July 2002 and on July 2003.



^{14}C, $\delta^{13}C$ and $\delta^{18}O$ were measured by different methods:

- ^{14}C by using the gas proportional counters and the liquid scintillation counting technique in Gliwice Radiocarbon Laboratory
- $\delta^{13}C$ by using the Elemental Analyzer Mass Spectrometer in UFZ Centre for Environmental Research, Leipzig
- $\delta^{18}O$ by using the Pyrolysis Gas Chronomatograph Mass Spectrometer in UFZ Centre for Environmental Research, Halle



In result of studies and measurements of isotopic composition of contemporary environment of Wigry Lake we have received the information about carbon cycle. As far as the isotopic composition of Wigry Lake is concerns, we have analyzed mean values and variations in ^{14}C, $\delta^{13}C$ and $\delta^{18}O$ among plants, lichens, differences of isotopic composition between investigated places of lake, dependences between content of carbon and $\delta^{13}C$. As far the carbon and oxygen isotopic compositions of plants, we have found out variations in $\delta^{13}C$ and $\delta^{18}O$ within plants, variations in $\delta^{13}C$ among whole material and cellulose, carbon isotopic composition of photosynthetically fixed carbon and syntaxonomic dependences.

Acknowledgments

$\delta^{13}C$ and $\delta^{18}O$ measurements were carried out within LEONARDO DA VINCI programme by Barbara Sensuła (Halle/Saale, Germany) and ^{14}C measurements within Silesian University of Technology BW /2004 grant (Gliwice, Poland).

Stable isotope geochemistry of quartz veins from the SW Alps: Evidence of higher paleoaltitudes and of rapid cooling by meteoric water infiltration

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Extensive quartz veins are found throughout the Central Swiss Alps. Temperatures of formation range from 450°C down to 150°C on the basis of phase equilibria, stable isotope thermometry and mineral stability. Vein formation started at 18-20 Ma and continued for over 10 My. Oxygen isotope data support an early vein quartz that was rock buffered, necessitating low fluid/rock ratios. A mechanism of differential pressure and silica diffusion – similar to lower temperature crack-seal mechanisms – is proposed for early vein formation. Fluid inclusions and hydrous minerals in late-formed veins have extremely low δD values, consistent with meteoric water infiltration. The change from rock-buffered, static fluid to infiltration from above can be explained in terms of changes in the large-scale deformation style occurring between 20 and 15 Ma. The rapid cooling of the Central Alps identified in previous studies may be explained by infiltration of cold meteoric waters along fracture systems down to depths of 10 km or more. To lower the geothermal gradient of a rock column by 200°C at 5 km over a 5 million year period requires only 0.1 cm^3/cm^2 of water penetration per year.

The low δD values of <–130 ‰ are far lower than modern meteoric water measured in the region, which range from –60 to –80 ‰. The lower fossil values are best explained in terms of elevation changes. δD values would be expected to be ~50‰ lower if the Central Alps were 3 km higher in the Neogene than today. This conclusion is supported by an earlier work of Jäger and Hantke (1983), where a paleoaltitude of 5000 meters was proposed on the basis of large erratic boulders found far from their origin.

Petrologic and stable isotopic studies on the Upper Crataceous travertine cone and red calcites (Vértes-Mts., Hungary) – Evidence for magmatic fluid influence

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A carbonate cone and red calcite debris occurrences were found in the Vértes Mts. (Transdanubian Central Range, Hungary). Petrographic and geochemical studies were carried out to determine the formation of the carbonates that can be clearly distinguished from the surrounding Triassic Main Dolomite.

The carbonate cone exhibits a special structure: vertically bedded carbonate characterize the middle part of the cone, whereas at the rims the beddings' dipping is less steep: 10-30°. The carbonate itself has a typical travertine texture: the spring cone consist of alternating massive, layered and porous calcite. The occurrence can be described as a travertine cone.

Thin sections were analyzed using EMPA techniques to determine the composition of the accessory minerals. The carbonate consists dominantly of calcite but minor amounts of xenomorphic zircon, xenotime and monazite were also found. According to the analyses we can conclude they are not derived from the surrounding dolomite.

Trace and rare earth elements (REE) analyses of bulk rock samples were carried out using neutron activation analysis (INAA). The carbonate cone is relatively enriched in LREEs particularly at the hypothetical vent-facies. A positive U anomaly was also observed. We can distinguish our trace element patterns from the Quaternary travertines of the area.

The $\delta^{18}O$ and $\delta^{13}C$ values obtained (24,5‰ and -8,5‰ respectively, average of 50 samples) are in agreement with those of the previously studied red calcite dikes widely occurring in the Transdanubian Central Range, but differs from the surrounding dolomite and from the younger travertines. A late Cretaceous age was suggested for the red calcite dykes based on the biostratigraphic evidence of the overlying sediments that contain red calcite fragments. The isotopic range of the samples studied indicates that magmatic CO_2 played an important role during the carbonate formation. Magmatic fluids can be associated with upper Cretaceous lamprophyre dykes recognized in the area.

The $\delta^{18}O$ values of travertine cone show a positive shift of about 1.5 ‰ from centre to rim suggesting that approximately 10°C temperature drop occured along the flow direction. Examinating the distribution of the $\delta^{13}C$ values we can distinguish concentric zones within the travertine cone: the $\delta^{13}C$ values increase from the vent facies towards to rim most likely caused by the rapid CO_2 degassing from the water.

On the base of trace element and isotope geochemistry, the formation of carbonate cone is not related to mobilization and precipitation of the surrounding dolomite, but it may rather be related to the upper Cretaceous magmatic activity of the area. Thus, it is one of the very rare pre-Cenozoic travertine occurrences.

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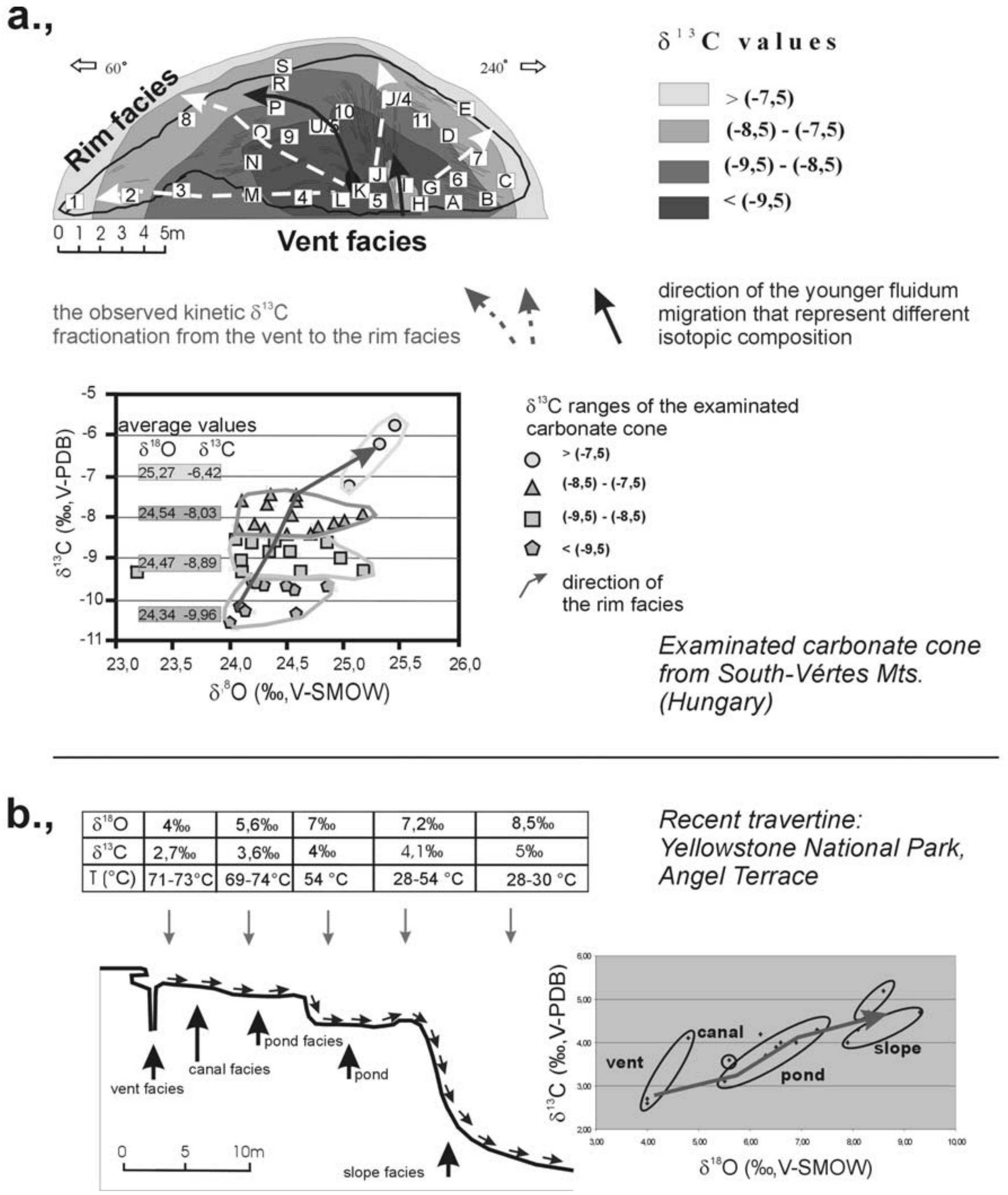

δ18O	4‰	5,6‰	7‰	7,2‰	8,5‰
δ13C	2,7‰	3,6‰	4‰	4,1‰	5‰
T (°C)	71-73°C	69-74°C	54 °C	28-54 °C	28-30 °C

Fig. 1 The measured stable isotopic composition and it's distribution of the examinated travertine cone (**a**.,) compared with a recent travertine occurrences (**b**., Angel Terrace,Yellowstone; Fouke et al. 2000). A remarkably positive shift can be recognised considering the stable carbon and oxygen isotope values from the vent moving to the slope facies at the Angel Terrace travertine (**b**.,). Similar trend is also typical for the examinated travertine cone (**a**.,) however more expressed δ^{13}C and less notable δ^{18}O changing can be seen at the South-Vértes (Hungary) occurrences. Arrows shows the direction from the central vent to the rim facies.

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Altitude carbon isotopic effect in peat-forming plants (*Sphagnum Sp., Politrychum Sp.*).

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Materials and methods

Samples of the recent peat (the uppermost 0-15 cm layer of the total organic mass including all leaving plants, collected in 2000) and recently growing plants (green alive elements of *Sphagnum Sp.* and *Politrychum Sp.* separately, growing in 2003) have been collected at the northern hillside of Karkonosze Mts. (south western Poland), along a transect from Śmielec Pass (1395m asl) to Jagniatków village (620 m asl). Sampling points were at different altitudes: 739, 834, 915, 1052, 1092, 1240, 1266, 1393m a.s.l. (see the sampling points shown on the map by Jedrysek et al. 2002, Skrzypek and Jędrysek 2004). Temperature and humidity sensors "HABO Oneset" have been located at the sampling points under trees (24 hour shadow). Automatic measurements of temperature and humidity with 1-hour interval, since 12 April till 15 October 2003 have been carried out. For isotope preparation, samples were defrosted and dried under vacuum. Afterwards, the plant material (*Sphagnum Sp, Politrychum Sp.* or recent peat) was combusted with CuO wire in a sealed quartz tube, under vacuum at 900°C. The CO_2 gas was cryogenically purified and then introduced to the mass spectrometer (Finnigan-Mat CH7 with a modified inlet and detection systems). The $\delta^{13}C$ values are quoted relative to the Pee Dee Belemnite international standard.

Results and discussion

Relatively good correlations in the combined systems of *Sphagnum Sp, Politrychum Sp.* and recent peat have been observed when eliminate the same two sampling points (1240, 1092 m asl) from each correlation system. Namely, the R^2 correlation factors in *Sphagnum Sp. - Politrychum Sp., Sphagnum Sp.* - peat and *Politrychum Sp.* - peat are 0.93, 0.95 and 0.91 (Fig. 1, 2, 3). We can not find any clear factor, but anthropogenic pollution (Jędrysek et al. 2002), responsible for the outstanding isotope ratios in the sampling points 1240 and 1092 m asl.

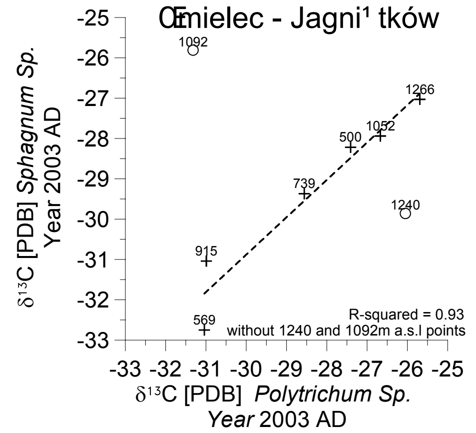

Figure 1. δ^{13}C *Polytrichum Sp.* and *Shagnum Sp.* correlation.

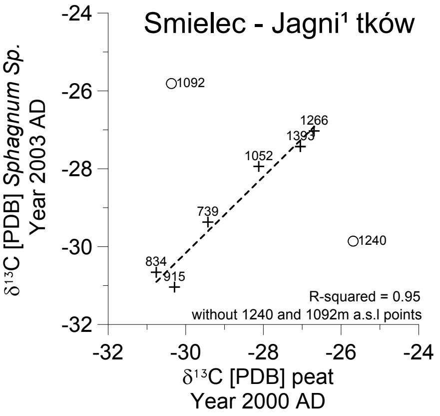

Figure 2. δ^{13}C recent peat and *Shagnum Sp.* correlation.

The high R^2 values in all the remaining points suggest that probably the same major factor(s) control(s) carbon isotopic composition in peat-forming plants. Moreover, this evidences that the primary carbon isotopic composition is not significantly modified during diagenetic processes in peat – *i.e.* peat keeps the original isotope record of plants. This is in agreement with other our results (Skrzypek and Jędrysek 2001).

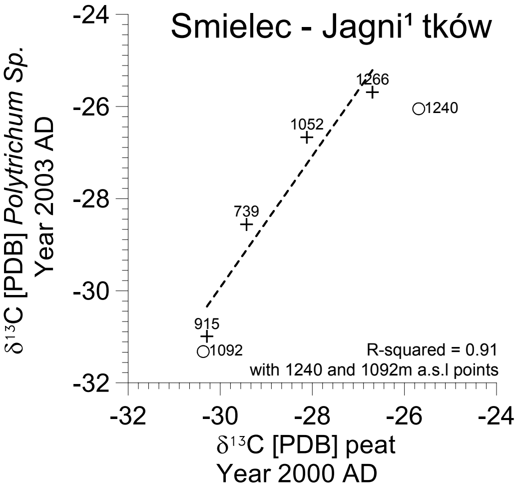

Figure 3. δ^{13}C peat and *Polytrichum Sp.* correlation.

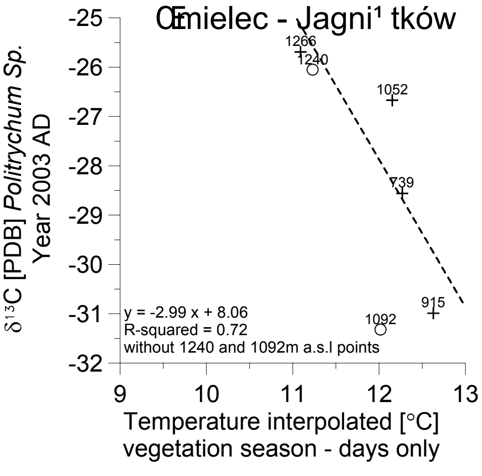

Figure 5. δ^{13}C (*Polytrichum Sp.*) – temperature of vegetation period correlation (day-light).

The correlation between δ^{13}C values in *Sphagnum Sp, Politrychum Sp.,* recent peat and average temperature (24 hours and day-light) of vegetation period have been analysed.

The same samples from altitudes 1092 and 1240 m show outstanding behaviour thus have been excluded from correlations. The correlation factors between the day-light temperature of vegetation period (T_{dl}) and $\delta^{13}C$ value is as follows: T_{dl} - $\delta^{13}C$ *Sphagnum Sp.* $R^2 = 0.68$, T_{dl} - $\delta^{13}C$ *Politrychum Sp.* 0.72, and T_{dl} – $\delta^{13}C$ peat equal 0.76 (Fig. 4, 5).

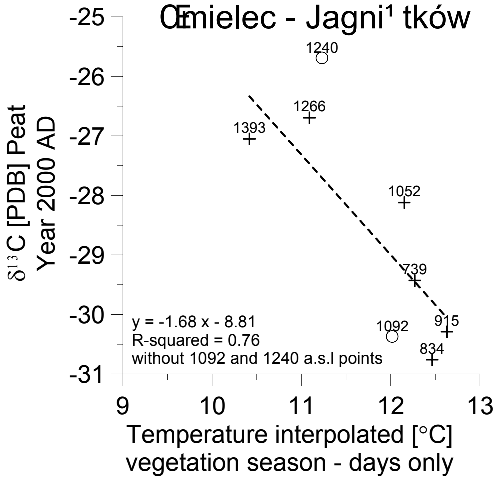

Figure 5. $\delta^{13}C$(peat) – temperature of vegetation period correlation (day-light – see the text).

The fairly good correlations between the temperature of vegetation periods and carbon isotopic composition of *Sphagnum Sp, Politrychum Sp.,* and peat confirm the thesis, presented earlier by the authors (Skrzypek and Jedrysek 2001, Jędrysek et al 2003) temperature is the most important factor controlling carbon isotopic composition of peat-forming plant tissue. It has been calculated that the variation of *Fq* value for peat is -1.68‰/ºC, *i.e.* 1˚C increase in daytime temperature (during vegetation period) results in -1.68‰ change in $\delta^{13}C$ value in peat. It seems that, in contrast to temperature, the humidity show no influence to carbon isotope composition of peat-forming plants. This evidence that humidity plays negligible role in carbon isotope fractionation of peat forming plants, and $\delta^{13}C$ peat profile do not represent any reliable humidity record.

Acknowledgments

This study was supported from the 2022/W/ING/03, 1017/S/ING/03-IX and 2P04G 004 26 grants.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Networking of a Rain-gauge with integrated isotope-sampling device and a spring monitoring station with automated event-sampling

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The system exists of an automatic rain-gauge and a measuring station at a spring with automatic sampling units. These two parts are linked up to a network via LEO-satellites. In the described configuration it is possible to run an event triggered automatic sampling, which is also remote controlled.

The precipitation station is designed to measure the rainfall and to offer the possibility to take samples for isotopic analyses of the total discharge during one month.

Precipitation measurement: Digital tipping bucket rain-gauge with a time resolution from one minute up to some hours (free of scaling) and a quantity resolution (depending on the type of bucket) from 0.1 or 0.2 mm rainfall. The amount of rainfall within a predefined time period is used as a trigger criterion for the measuring unit at the spring. This trigger causes only the sampling of a reference sample.

Sampling application: For isotopic analyses it is necessary, that no part of the precipitation can evaporate. Therefore in this application the containers where the precipitation are stored, can be opened and closed. This procedure is working automatically. When the rainfall starts (=the moment of the first tipping), the container is opened. After the rainfall it is closed again. The time of delay can be chosen individually (for instance 1 to 10 minutes).

To get correct samples of one month, a second valve is changing the flow path between the two containers exactly at the beginning of the month.

The schematic construction of the isotope sampling device is shown in Fig. 1.

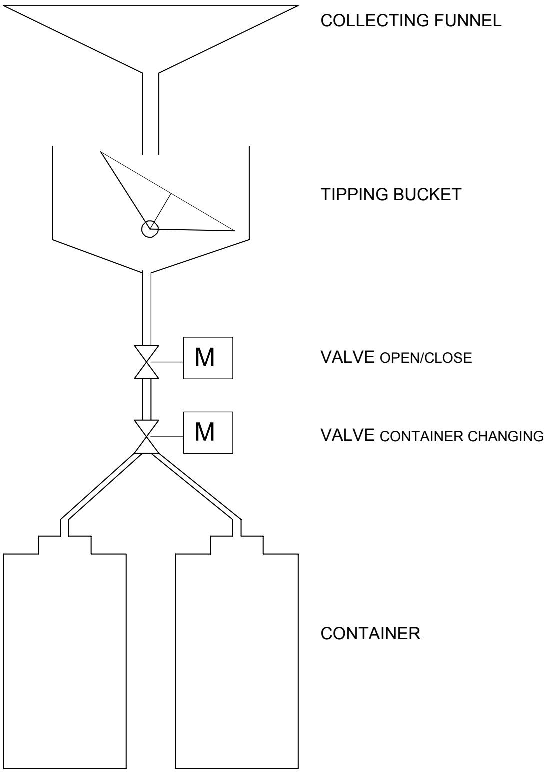

Fig. 1. Scheme of the automatic isotope-sampling device.

Both valves are controlled by the data-logger. Apart from precipitation also other parameter like temperature, wind speed, radiation, and so on can be stored.

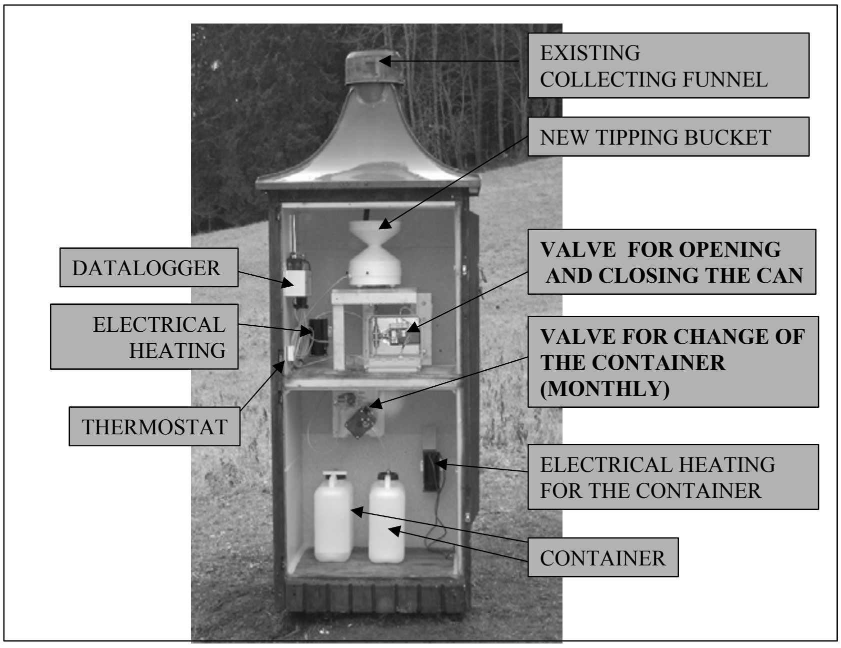

Fig. 2. Automatic precipitation station with integrated isotope-sampling device.

The picture shows a station of the Zentralwasserversorgung Hochschwab Süd, rebuilt with the digital equipment and the isotope sampling device.

The whole application can be mounted in existing measuring stations, without changing the existing collecting funnel (as shown in Fig. 2). This is important for the continuity of the measurement at an existing station.

To avoid large changes of temperature of the sampled water, the containers can be isolated. The station must be heated in such a way, that the sample is not freezing. A simple funnel heating is not enough. The heating can be done with gas or electricity. The electrical heating can be regulated by a thermostat. In stage of development are funnel-heating with Peltier-elements. This devices are also able to cool the collecting funnel during hot periods.

The system (without the heating) can be supplied with solar panels and supplemented with remote data transfer systems like LEO-satellites, GSM or telephone.

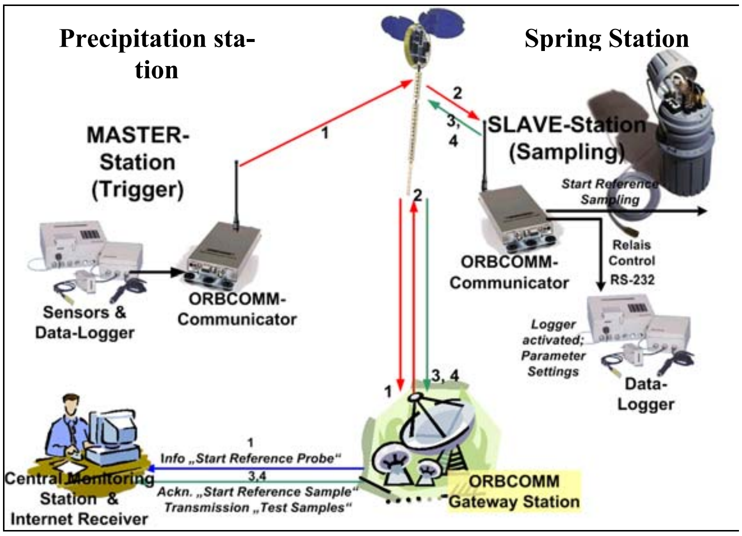

Figure 3: Prototype Block Diagram of event-triggered water sampling using satellite transmission

Spring measurement: At the spring different parameter can be recorded with a data-logger. One of these parameters can be used as second trigger criterion. In our test, the changing of the gauge height within a predefined time period is used as second trigger. If both trigger criterions are happening in a chosen time period, the periodic event sampling is started.

The schematic block diagram is shown in figure 3.

In the following, the important features and data streams are described. As it is shown, all activities of the two stations can be observed at the “Central Monitoring Station” in the office but also via GPRS somewhere outside.

- Triggering station(s): This meteorological station records e.g. rainfall with a time resolution down to one minute and sends data samples periodically (1) to a central monitoring station. Additionally, it automatically derives a trigger criterion from the recorded amount of e.g., precipitation. The station transmits via satellite activation data-set to all sampling/measuring stations (1) and to the central monitoring station.
- Sampling station(s): When the activation data-set is received, the automatic sampling unit takes the reference sample. This status is sent to the central monitoring station (2). Rainfall in the catchment area need not produce a discharge event at the monitored spring immediately, therefore, a second triggering criterion can be derived from the gauge height at the sampling station. As soon as this trigger-level is exceeded, a second automatic sampling device starts the periodical event sampling with a pre-selected time interval. This status is also sent to the central monitoring station (2).
- Central monitoring station: It comprises a specifically developed email-client to decode the com-pressed measurement data-sets which are transmitted from the gateway earth station of the satellite system as emails (1). The decoded data are stored in a central data-base, graphic visualization is be provided (2). A remote Internet access to that central monitoring station is provided so that the re-searcher can also monitor its stations from outside the laboratory, e.g. via GPRS (1,2,3).

In a next step triggering-events will also be derived from on-line measured quality parameters, which can be used as part of an early warning system or a Decision Support System (DSS). Because of data compression, satellite transmission costs for the new system can be expected to be considerably lower than manual operation. Depending from the used automatic sampling units this equipment can be used for isotope sampling.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

Origin of nitrate in groundwaters of Kalahari, Botswana

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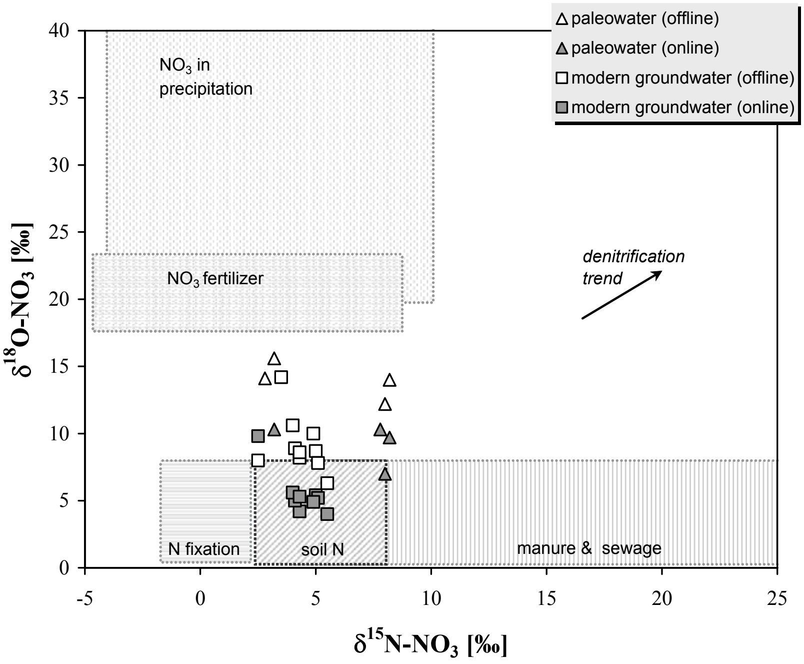
In groundwaters from Kalahari, Botswana, elevated nitrate concentrations exceeding the WHO-guideline value of 50 mg/L have been found in mostly uninhabited semi-arid areas. Here we present first results of an isotope hydrological investigation with main emphasis to identification of input factors and the origin of that nitrate in groundwater.

The investigation area is located on the eastern fringe of the Kalahari between Serowe and Orapa, Botswana. Mean annual rainfall in the investigation area is about 450 mm/yr. The area is characterized by a flat topography at about 1200 m above sea level. Groundwater samples were taken from the Triassic Ntane sandstone aquifer, which comprises the main aquifer of the Karoo strata in the investigated area. The aquifer is mostly confined by fractured Early Jurassic Stormberg basalts and an extensive cover with Kalahari sands.



According to their significantly different ^{14}C contents, the investigated groundwaters can be divided into two distinct groups: modern groundwaters (40 to 90 pmC) of

Ca-Mg-HCO_3-Cl type and Na-HCO_3 type paleowaters (< 15 pmC), respectively. The high radiocarbon contents of the first group clearly confirm the presence of active recharge in the order of 1-5 mm/yr (Verhagen 1991). Only the modern groundwaters are affected by high nitrate concentrations. According to nitrate stable isotopes (Fig. 1), natural accumulation processes in soil (Heaton et al. 1983; Aranibar et al. 2003; Walvoord et al. 2003) seem to play the important role concerning the source of nitrate. The lack of an anthropogenic nitrate pollution in the investigated groundwaters indicated in Fig. 1 is in accordance with long residence times in the unsaturated zone, as suggested by tritium below detection limit in all groundwater samples.

Within the ^{14}C containing (> 40 pmC) modern groundwaters, nitrate concentrations positively correlate with ^{14}C content. If not due to anthropogenic activities, the decreasing nitrate concentration with increasing (corrected) ^{14}C age (up to 3.000 years) must be a consequence of a change in nitrate leaching and/or of a change in recharge conditions.

The impact of different recharge conditions is confirmed by a strong linear correlation of nitrate with dissolved ^{20}Ne content (Fig. 2). ^{20}Ne is found in excess in all groundwater samples, which is due to excess air dissolved in course of the recharge process. The extend of excess air is influenced by the rate and extend of recharge and therefore may be used as an indicator to distinguish between dry and wet infiltration conditions (Heaton et al. 1983; Stute and Talma 1997; Beyerle et al. 2003). High nitrate contents correspond to low ^{20}Ne excess values, which sug-gest a slow re-charge where ^{20}Ne concentrations are maintained at so-

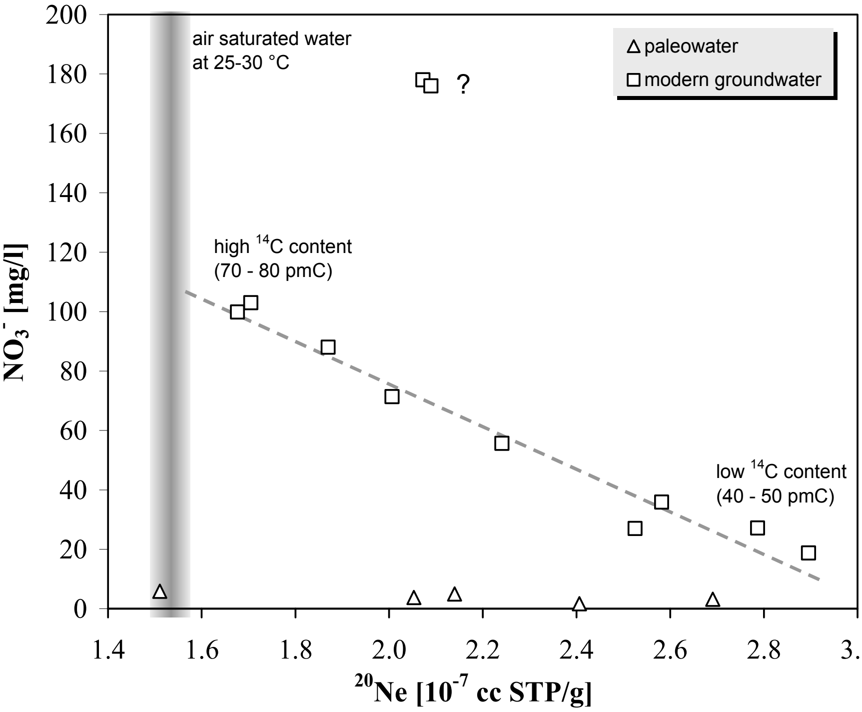


Fig. 2. Nitrate and ^{20}Ne contents of Kalahari groundwaters out of the Ntane sandstone aquifer. Today's low recharge rates yield low ^{20}Ne and high nitrate contents as end member of the mixing line with high ^{20}Ne/low nitrate containing groundwaters recharged under more humid conditions.

lubility equilibrium. Low nitrate on the other hand is connected to recharge under wet conditions, where air is captured below the water table.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

The Tisza-project – challenges and perspectives

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The goal of the national project entitled Hydroecology of River Tisza and Upper Tisza-Region (NKFP-3B/0019/2002) is to provide scientific foundation of the hydroecological state assessing, monitoring and databank organising program of River Tisza and Upper Tisza-Region supplementing with pilot-projects of practical realisation. In the first phase of this project our task was the investigation of the origin and mixing of water in the catchment area of Main-channel Lónyai. For this aim stable isotope ratios (δD, $\delta^{18}O$, $\delta^{15}N$, $\delta^{34}S$, $\delta^{13}C$) were measured in water and sediment samples taken from the catchment area of Lónyai. Three samples were taken from the main channel, and two side channels were represented by 2-2 samples.

Special emphasis was placed to the water isotopes tritium and ^{18}O because of their specific potential in addressing water balance, dynamics and interrelationships between surface and groundwater in river basins and catchment areas. The most negative $\delta^{18}O$ values were measured near the sources of the two side channels: both of them had $\delta^{18}O = -9.7‰$. This value is characteristic for the deep groundwater in Nyírség. In a distance of several kilometers from the sources the water in both of the channels had less negative delta values than at their origin. It means that the channels were fed by direct overland runoff during their route and no subsurface water was added.

Main-channel Lónyai carries large amount of communal wastewater to River Tisza. The measured delta-values showed a large inflow from subsurface water body between Kék and Ibrány. The $\delta^{15}N$ value of the dissolved ammonium measured at Ibrány indicated presence of manure, so the water came from communal wastewater. The $\delta^{18}O$ value of the water sample taken near the channel-mouth showed that the water was mainly of subsurface origin with a small contribution of overland runoff, and the effect of evaporation was insignificant. The tritium content of this water was ~0.1 Bq/l. The annual average of tritium concentration in precipitation in Debrecen, as well as the tritium concentration measured in River Tisza at Tiszabecs is about ten times higher: ~1 Bq/l. It supports the conclusion drawn from the stable isotope results: the water used for communal purposes originates from old, deep subsurface water body. C, O and S isotope ratios measured in the sediment samples were similar to each other, mixing of organic and inorganic compounds could be observed.

Diurnal variations of δ^{13}C and concentration of atmospheric and soil carbon dioxide in a meadow site

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Diurnal (24-hours) variations of carbon isotopic composition and carbon concentration in the air over a meadow and also in the soil were investigated during late Spring (11 – 12 June 2003). As the study site we have chosen a flat meadow covered with high grass, before mowing. It was located in the Bystrzyca river valley, on the left side of the river, 100 m from the waterside trees, 600 m from the road and 500 m from the nearest farm buildings of the Żabia Wola village, near Lublin. The sampling site was situated in the grass, the height of which was about 0.7 m, in the middle of rectangular meadow (200 m x 50 m). The atmospheric conditions during sampling were steady; almost cloudless and windless, the atmospheric pressure was 100 kPa at 203 m above sea level. The air and soil temperature varied from 9 to 25 ^{o}C and from 14 to 17 ^{o}C, respectively. The soil was dry; no rain falls were recorded over three weeks prior to observation. The samples of atmospheric air were sucked into evacuated ampoules from three horizons: near the soil (0.05 m), between the grass (0.5 m) and above the meadow (2 m) every two hours. At the same time samples of soil air were collected from two horizons: -0.1 m and –0.5 m. Soil air was slowly sucked into 50 ml syringes. During sampling the temperature of air above the ground and of the soil were measured too. The samples were immediately delivered to the laboratory, where the CO_2 was extracted and analysed mass-spectrometrically (Dudziak, and Hałas, 1996; Szaran, 1998; Szaran et al., 2002). The results are presented in figures.

Results for atmospheric air

1. The isotopic composition is a very sensitive indicator of biogenic activity, more sensitive than CO_2 concentration.

2. After the twilight the CO_2 concentration increases and the amount of ^{12}C increases too, tending to amount of ^{12}C in the soil air (the maximum is reached before a dawn). After the dawn the CO_2 concentration decreases and the amount of ^{12}C decreases too, and $\delta^{13}C$ tends to the value –8‰.

3. The maximum values of CO_2 concentration in the atmospheric air were noticed near the soil, also the concentration of ^{12}C near the ground was the highest.

4. The lowest contents of ^{12}C and the lowest CO_2 concentration were noticed in the air within the grass at 0.5 m level above the ground. Also the variation of the CO_2 concentration were the smallest on this level.

5. The largest variation of the CO_2 concentration was noticed in the air near the ground.

6. A very good correlation was noticed between $\delta^{13}C$ and $1/CO_2$ concentration at the horizon of 2 m above the ground ($R^2=0.984$) and near the ground ($R^2=0.932$), whereas within the grass the correlation was rather weak ($R^2=0.47$).

Results for soil air

1. CO_2 concentration in soil air and ^{12}C contents at the depth of 0.5 m were higher than at the horizon of 0.1 m and in the atmospheric air.

2. The relative variation as well as the CO_2 concentration and ^{12}C contents were insignificant in the soil air.

3. The correlation between $\delta^{13}C$ and $1/CO_2$ concentration in the soil air was very weak. The squared correlation coefficients were $R^2=0.30$ and 0.02 at depths 0.1 m and 0.5 m, respectively.

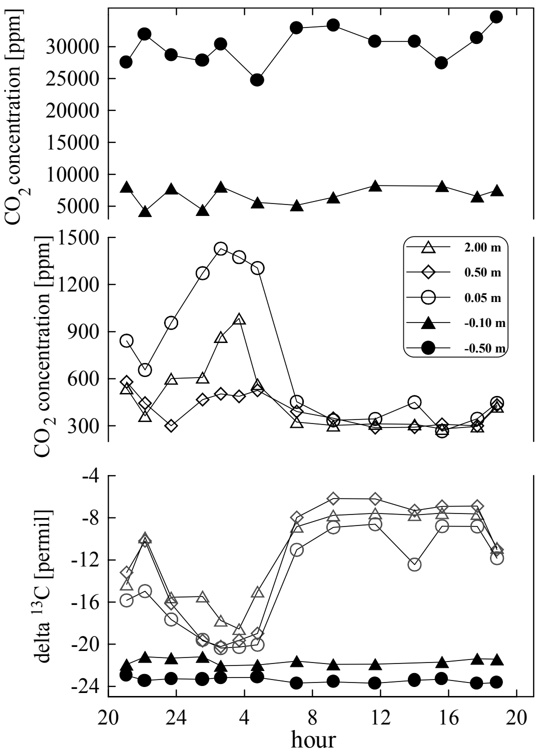

Fig. 1. Diurnal variations of concentration and carbon isotopic composition in soil and atmospheric carbon dioxide at various horizons, see legend.

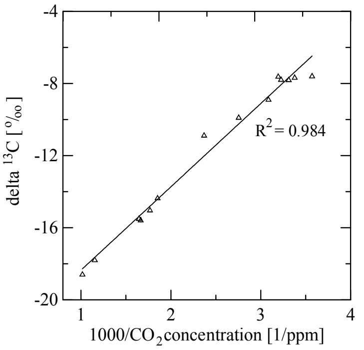

Fig. 2. Correlation between carbon isotopic composition and reciprocal concentration in atmospheric air (2 m).

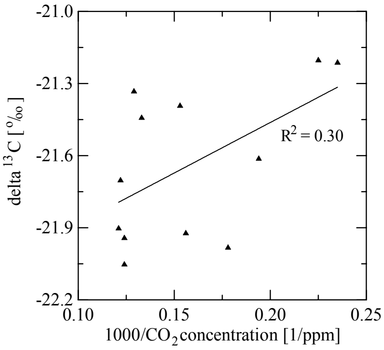

Fig. 3. Correlation between carbon isotopic composition and reciprocal concentration in soil air (-0.1 m).

Conclusion

The strong diurnal variations and the correlation between $\delta^{13}C$ and CO_2 concentration in the atmospheric air indicate a mixing line, from which $\delta^{13}C$ of the biogenic CO_2 may be inferred. The extrapolation of the straight line to zero value of the 1/(CO_2 concentration) yields $\delta^{13}C$=-23.0 ‰. Rather small diurnal variations are characteristic for a dry soil, thereby $\delta^{13}C$ is weakly correlated with CO_2 concentration.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

$\delta^{13}C$ in α-cellulose from oak latewood 1631-1765 AD

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This work presents $\delta^{13}C$ measurement using α-cellulose from oak latewood of annual growth rings (*Quercus robur L.*) 1631-1765 AD.

In Gliwice (Pawełczyk *et al.*, 2004) we used a modified technique based upon the sodium chlorite oxidation method of Green (1963) utilities an ultrasonic bath. This technique yields a material with sufficient homogeneity as required for isotopic composition measurements. The diagram of α-cellulose extraction from wood samples can be briefly presented as follows (Robertson and Waterhouse, 1998):

$$\text{wood} \xrightarrow[\mathrm{CH_3COOH}]{\mathrm{NaClO_2}} \text{holocellulose} \xrightarrow{\mathrm{NaOH}} \alpha\text{-cellulose}$$

To receive holocellulose a sample was put into a beaker filled with distilled water, sodium chlorite and acetic acid, in amounts as below.

Reagent	*Amount*
Wood shavings	1 g
Distilled water	175 ml
Sodium chlorite	2.5 g (per addition)
Acetic acid [80%]	1.7 ml (per addition)
10% sodium hydroxide	75 ml
17% sodium hydroxide	67 ml

The beaker was covered with glass and placed in an ultrasonic bath (70°C). Five times, one an hour, acetic acid and sodium chloride were added. The beakers were taken out and the solution was removed. Holocelullose was rinsed, first with hot distilled water and then with cold distilled water. Its colour was checked – holocellulose should be quite white. In case of tinge the cleaning was repeated. Holocellulose was dried in 70°C.

To holocellulose 10% solution of NaOH was added and beaker was placed in an ultrasonic bath for 45 min (about 70°C). After that sample was rinsed with cold distilled water. The samples were put into beaker with 17% solution of NaOH and they were subjected to ultrasonic for 45 min in the room temperature. α-cellulose was rinsed, first with 17% solution of NaOH, next with big amount of distilled water, then with 1% solution of hydrochloric acid and finally with big amount of cold distilled water (until the solution was neutral). α-cellulose was dried in 70°C.

For $\delta^{13}C$ measurements with mass spectrometer CO_2 was prepared from the dried α-cellulose. The cellulose sample was placed into individual pyrex tubes with copper oxide. The tube, in which 10 mg of cellulose, 1300 mg of preheated CuO and 150 mg silver wool are placed, was sealed under vacuum. Next, it was put into a metal thimble and heated in muffle furnace for 18 hours in the temperature of 450°C. The resulting gases were separated cryogenically and the CO_2 was collected.

In $\delta^{13}C$ α-cellulose time record the cooling between *ca* 1650-1700 AD is clearly visible. Comparison of this record with $\Delta^{14}C$, width tree rings, sunspot numbers and $\delta^{13}C$ in nitrate cellulose indicate on correlation or anti-correlation of these records according to predictions. Results of $\delta^{13}C$ measurements in nitrate cellulose from the paper Krąpiec et al., 1998) were taken.

Acknowledgments

This work was supported by EU grants No. EVK2-2001-237 (ISONET) and by State Committee for Scientific Research grant SPB-12/RMF-1/2003.

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Changes of methanogenic pathways in freshwater sediments – an incubation experiment

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Introduction

Methane is one of the latest products of microbial decomposition of organic matter. It is produced in marine or freshwater anaerobic sediments mainly due to acetate fermentation or CO_2 reduction pathway. In recent studies the carbon isotope analysis are commonly used to distinguish methanogenic pathways and to establish sources of methane. The $\delta^{13}C$ value is also considered in mass balance calculation of methane in the atmosphere. Such calculation is difficult because carbon isotope composition of methane undergoes spatial and temporal variations (e.g. Jędrysek 1995, Hornibrook 2000). The reason of $\delta^{13}C(CH_4)$ variations in particular environments is still enigmatic, but four main factors are considered to be responsible of that: 1) changes of methanogenic pathways, 2) availability of substrates, 3) temperature variations and 4) spatial distribution of labile organic carbon in depth profiles of sediments or water reservoirs.

In this paper we consider the changes of methanogenic pathways relative to the availability of labile organic carbon and time of decomposition of organic matter in freshwater sediments. Miyajima et al. (1997) has evidenced that increased recalcitrance of soil organic matter results in greater production of CH_4 through the CO_2 reduction pathway in tropical wetlands. The same conclusion was done by Hornibrook et al. (2000) in freshwater wetlands, who suggest that the lower rate of methanogenesis based on acetate fermentation is a result of decrease of labile organic carbon with increasing recalcitrance of biodegraded organic matter. To test this thesis we incubated freshwater sediment under long time interval (570 days). The studied incubator is near closed system, because the sediment with organic matter was put in it once. Only gases produced in the sediment would undergo the exchange with atmosphere during the incubation and sampling. The accept procedure of incubation allowed tracing changes in substrate availability for methanogenesis due to increase of recalcitrance of organic matter enclosed in the incubated sediment.

Methods and results

The data presented come from one incubator. The incubation method and the source of incubated sediment were described by Szynkiewicz et al. (this volume). During 570 days of incubation, in one month intervals, the concentrations and $\delta^{13}C$ values have been analyzed in:

- methane in pore gases in the sediment,
- organic matter in the sediment
- DIC in the sediment/water interface.

After each sampling action, the sediment was mixed with water column to remove the CH_4, which still left in the sediment as well as to homogenize DIC concentration and $\delta^{13}C$(DIC) in the water column and sediment.

In the course of 570 days of the incubation, the permanent decrease of CH_4 concentration (from 86 to 39 %) and increase of $\delta^{13}C(CH_4)$ values (from –68.90 to –61.37 ‰) in the incubated sediment have been observed (Fig. 1). However, the concentration of organic matter in the sediment varied independently from 1.02 to 2.03 % (Fig. 2). The $\delta^{13}C$ value of organic matter showed very narrow range from –28.10 to –27.54 ‰. The concentration of DIC in the sediment/water interface showed weak decreasing trend (R = -0.47; Fig. 3) and varied widely along the incubation time from 100.68 to 216.62 mg/l. However, the $\delta^{13}C$(DIC) value showed permanent decreasing trend (R = -0.85; Fig. 3) from –6.33 to –12.04 ‰.

Discussion

Methane originated from acetate fermentation shows higher values of $\delta^{13}C$ (from –65 to –50 ‰) as compare to the methane from CO_2 reduction (from –110 to –60 ‰). The acetate is a fermentative product of easy degradable organic compounds and represents fraction of labile organic carbon in sediments. It is also well documented that acetate is probably the main substrate for methanogenesis in freshwater sediments. In our opinion, during the incubation, the acetate fermentation was the main methanogenic pathway. The obtained $\delta^{13}C(CH_4)$ values were typical for this process. We did not measure the acetate concentration and $\delta^{13}C$ value of the acetate, but the observed increase of $\delta^{13}C(CH_4)$ and decrease of methane concentration (Fig. 1) may be resulted from depletion of acetate in the incubated sediment.

There is no evidence of methanogenesis due to CO_2 reduction. Moreover, increasing recalcitrance of organic matter with time of incubation did not cause the change of methanogenic pathway toward CO_2 reduction, like we expected. This pathway involves higher carbon isotope fractionation and $\delta^{13}C(CH_4)$ values are distinctively lower than these from acetate fermentation. The $\delta^{13}C(DIC)$ values at the sediment/water interface became more negative along the incubation (Fig. 3). For that reason we are convinced that changing of methanogenesis toward CO_2 reduction would reflect in lower $\delta^{13}C$ value of methane at the end of the experiment. However, the obtained data evidenced that methanogenesis was probably dependent mainly on the acetate pool in the incubated sediment, which became enriched in ^{13}C along the entire incubation. In spite of this, it is not clear why the concentration of total organic matter showed higher variations and did not decrease along the incubation (Fig. 2). We suspect, that probably some microbial processes, especially in water column, could influence the supply of fresh organic matter. On the other hand, it is enigmatic why these processes did not influence the amount of acetate in the incubated sediment.

The presented data suggest, that activation of methanogenesis due to CO_2 reduction probably requires higher concentration of DIC (CO_2 or HCO_3^- ion) in the sediment. It is usually considered, that limiting factor of this pathway is H_2 production in the sediments. However, it could rather influence for methane concentration in the pore gases of sediment along the entire incubation. Even though, $\delta^{13}C(CH_4)$ should express more negative values relative to decreasing trend of $\delta^{13}C(DIC)$ values along the incubation.

The important role of DIC concentration in the process of methanogenesis due to CO_2 reduction was also confirmed by the incubation of the same sediment under elevated concentration of SO_4^{2-}. The intensive oxidation of acetate by sulphate reducers in this incubator involved higher production of CO_2, what activated methanogenesis due to CO_2 reduction (Szynkiewicz et al. – see this volume) and the availability of H_2 was not the limiting factor in this case.

The CO_2 reduction pathway is commonly observed in deeper profiles of sediments. They are generally characterized by higher concentration of pore gasses collected in various stages of microbial decomposition of organic matter. In our experiment the concentration of DIC was always diluted after each sampling due to mixing the water with sediment. Probably, this procedure limited DIC concentration, thus also the CO_2 reduction. For that reason methanogenesis was mainly dependent on the availability of acetate in the incubated sediment.

Conclusion

1. The acetate fermentation was the main methanogenic pathway in the incubated sediment.
2. Increasing recalcitrance of organic matter along the time of incubation did not cause the change of methanogenic pathway toward CO_2 reduction.
3. Probably, higher concentration of DIC is required to activate the CO_2 reduction pathway. Such conditions are common in deeper profiles of sediments, where the produced gases are stored for a longer time.

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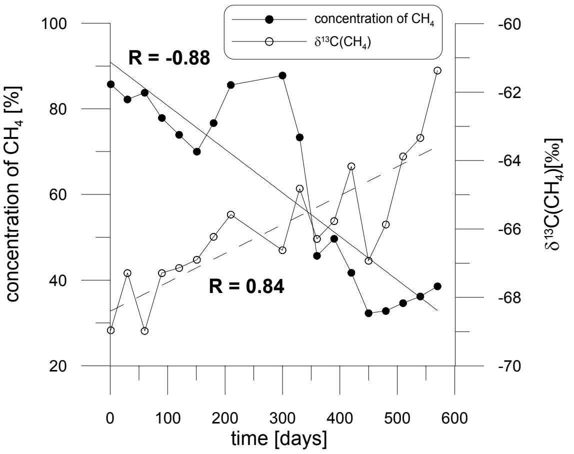

Fig. 1. Variations of methane concentration and their $\delta^{13}C$ value along the 570 days incubation.

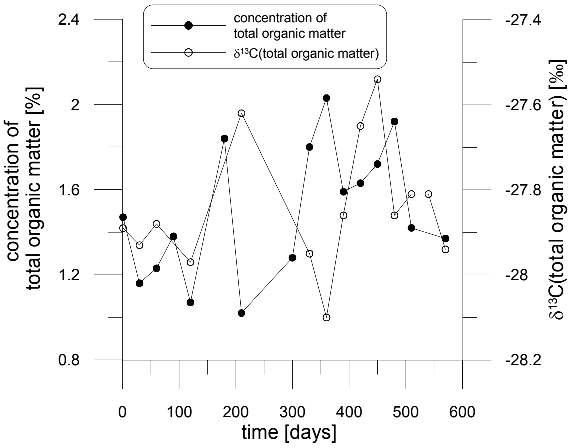

Fig. 2. Variations of total organic matter concentration and their $\delta^{13}C$ value along the 570 days incubation.

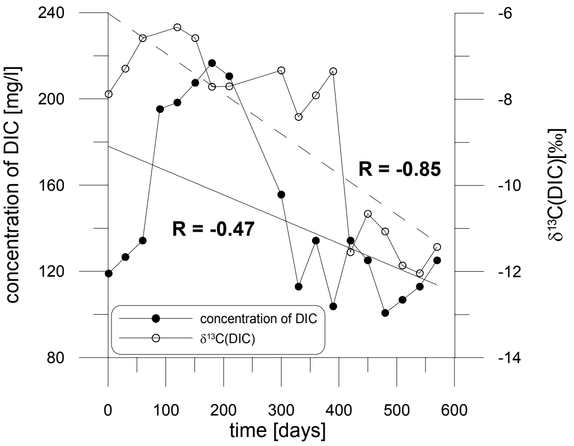

Fig. 3. Variations of DIC concentration and their $\delta^{13}C$ value in the sediment/water interface along the 570 days incubation.

Lateglacial – Middle Holocene stable isotope records in two coeval stalagmites from Bihor Mountains, NW Romania

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Two stalagmites (S22 and S117) from V11 cave (Bihor Mountains, NW Romania) have been sampled for stable isotopes for the interval Late-glacial to Middle Holocene. V11 Cave is located in the Bihor Mountains at an elevation of 1254 m. It is situated in an area with alpine climate, mean annual temperature of around 4°C, 1400 mm/year precipitation and an average of 6 months of snow. The two stalagmites were collected from a passage, 200 m away from the cave entrance and some 60 m below the surface. The passage has no noticeable airflow and humidity is close to 100%.

Both stalagmites consist of yellow-brown low-Mg calcite, generally with columnar fabric. TIMS dating of the two stalagmites shows six growth periods occurring between 136 and 5.6 ka, separated by hiatuses. The last depositional interval occurred between 14.5 - 5.6 ka for S22 and 16 - 6.1 ka for S117 (Tămaş & Causse 2001). Based on high resolution TIMS dating and on morphological evidence, we assumed that S22 stalagmite growth was not interrupted during the interval sampled for stable isotope studies. S117 has a small growth hiatus between 10.9 and 10.3 ka, probably due to a slight changing of the feeding point.

Stable isotope analyses were performed at intervals of 2 mm for S22 and 1 mm for S117. The age model presented is based on 12 ages for S22 and 10 ages for S117, leading to calculated growth rates of 11.2 - 91.6 mm/ka for S22 and 2.8 - 82.8 mm/ka for S117. Two tests for kinetic isotopic fractionation were performed on each stalagmite. The maximum $\delta^{18}O$ variations within the growth layers were 0.49‰ and 0.53‰ (S22), and respectively 0.18‰ and 0,26‰ (S117).

The $\delta^{18}O$ and $\delta^{13}C$ profiles consist of 306 samples. For S22, $\delta^{18}O$ values range between -9,25‰ and -7,23‰ (VDPB) and $\delta^{13}C$ between -4.15‰ and –8.83‰. Isotope variations recorded in S117 are –9.3‰ - –6.69‰ for $\delta^{18}O$ and -9.1‰ - -5‰ for $\delta^{13}C$. The $\delta^{13}C$ and $\delta^{18}O$ isotopic profiles show no correlation during the Late-glacial, but they slightly correlated during the Holocene.

Carbon isotopes show an increasing trend from termination I, with high values (-4.15‰ -5‰) during the Younger Dryas, and then decrease by almost -3‰ at the Younger Dryas/Preboreal transition. The oxygen records drops with 0.6‰ to –1‰ at the Allerod/YD transition, but they remain low during the whole Preboreal. A corresponding increase is recorded at around 10.2 - 10 ka BP. From 10.3 ka onwards, both the $\delta^{18}O$ and $\delta^{13}C$ profiles have a slightly increasing trend, but less oscillations.

The stable isotope analysis of the two stalagmites from NW Romania provide a terrestrial record which reflect Late-glacial and Holocene environmental changes. The profiles can be correlated with other terrestrial records, such as stalagmites and lacustrine sediments.

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Tracing anthropogenic effects on the urban water system using stable isotopes

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Urban water systems are polluted by diffuse and direct contributions from anthropogenic activities. Besides industrial contaminants like aromatic and chlorinated hydrocarbons and other persistent organic compounds, the urban aquatic environment is increasingly polluted by low concentrated but high eco-toxic compounds as pharmaceuticals, fragrances, and plasticizers, most of which are under suspicion of having disrupt endocrine functions. Therefore, these contaminants will have a long-time impact on the urban ecosystem and on human health when released by surface waste water outflows and seeping subsurface waste waters. For assessing the impact of human activities on the urban water system, isotope analyses seem to be a useful tool to estimate the origin of these contaminants, possible transformation processes ongoing within the aquatic environment, and their distribution within the urban water system. Among other indicators we investigated the isotopic signatures of water (H, O) and dissolved substances (sulfate, DIC, nitrate).

In 2001 we started investigations of the anthropogenic effect of the city of Halle on the urban water system. Halle is located at the river Saale which acts as the major draining system collecting different inputs along its city traverse from south to north. At the northern fringe of the city the treated waste water of the whole city flows into the river.

The river water reflects the meteoric water signature of the area with mean δ^2H and δ^{18}O values of about -60 ‰ and -8.6 ‰ and a typical seasonal variation. The isotopic signature of dissolved sulphate from the Saale river and its tributary Weisse Elster differs clearly due to the different origin of sulphate in their respective sub-catchments. Palaeozoic evaporates occurring upstream of Halle influence the dissolved sulphate of the Saale giving enriched δ^{34}S values > 9 ‰ whereas sulphate of the Weisse Elster is characterized by the Quaternary sediments more depleted in ^{34}S. Both rivers join just before entering the city region.

Treated waste water with $\delta^{34}S < 2$ ‰ constitutes a third source of sulphate, which mixes into the Saale river at the northern border of the city.

Dissolved inorganic carbon varies in $\delta^{13}C$ between -10 to -16 ‰ which indicates degradation of organic matter and gas exchange with atmosphere.

Nitrate dissolved in the river water can be attributed to at least two distinct sources. Treated waste water with enriched $\delta^{15}N$ values of > 12 ‰ is typical for septic waste waters. In contrast to the waste water signature, the nitrate of both rivers is influenced by seasonal nitrogen input from the rural catchments showing a range of 5 to 12 ‰ as can be expected for nitrogen from agriculturally used soils. Denitrification processes presumably contribute to the enrichment in $\delta^{15}N$ occurring during the summer season, although not confirmed yet (e.g. by $\delta^{18}O$ of nitrate). According to the geochemical conditions, denitrification also can be expected in the urban groundwater which is the focus of the current investigations towards assessment of the sources and the fate of pollutants within the urban water system.

Flow paths, mixing processes and exchange reactions in organic contaminated groundwaters of industrial sites: insights from the H and O stable isotope composition of water and that of dissolved organic and inorganic C

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Introduction

Contamination of soil and groundwater by organic pollutants is a serious environmental problem. In particular, former industrial sites may pose special problems because of the high toxicity of their pollutants. Because of the high toxicity of the pollutants it is important to characterize the hydrological situation in order to be able to asses the dispersion of the organic contamination. Groundwater pollution is commonly evaluated in terms of analyses of anions, heavy metals and/or organic substances as well as adding chemical tracers to the groundwater and evaluating the hydrologic situation via time-sequence analyses of the tracers and/or via pump-experiments. Many of these measurements of chemical tracers may be influenced by sorption processes or chemical reactions and can, therefore, give a distorted picture of the contamination. In contrast, stable isotope studies of hydrogen, oxygen, and carbon in water can potentially be used as natural tracers that are not influenced by sorption processes. Furthermore, under most low temperature conditions the H and O isotope composition of water is also not influenced by chemical reactions within the aquifer. It is known from several studies, that the analyses of hydrogen and oxygen isotopes of water provide information on recharge areas and mixing processes of different water bodies. Seasonal variations of the isotopic composition of precipitation and groundwater can give additional information on infiltration times, flow paths and flow velocities. In addition, the carbon isotope composition of dissolved inorganic carbon (DIC) can provide a tracer for anthropogenic contamination, given that the natural system can be characterized too.

The use of stable isotope studies of hydrogen, oxygen, and carbon in groundwaters as natural tracers for the hydrogeologic system is exemplified here on the basis of a case study from a former gas production plant in southern Germany. Extensive destruction of this site during the Second World War caused severe damage to the plant that, in addition to production-specific leakes, has led to extensive contamination of sediments and groundwater by organic residues of the gas production. The pollution, mainly tar and its distillates, was recognized in 1970 during excavation for a liquefied natural gas storage tank and the site is presently under investigation for remediation.

Geological and hydrogeological setting

The site is located in the south-west of Germany, in the valley of the Neckar river, a tectonically defined graben forming part of an extensive fault system that strikes NW-SE. The main aquifer is a Quartemary fluvial gravel deposit overlain by silty-clayey, organic matter-bearing alluvium. Above it, artificial fillings made up of building rubble and gravel have been deposited. The Quarternary gravel deposit consists of Jurassic marine carbonate pebbles and it is the first of three aquifers. Tar-oil contamination is located within this aquifer. The flow direction of groundwater is parallel to the adjacent river with a flow of about 2.5 m/d. Water in the Quarternary aquifer is generally confined. Underneath the Quarternary aquifer are two further aquifers that complicate the hydrogeologic situation. The second "Gipskeuper" aquifer is a dolomitic, gypsum-bearing clay- and siltstone of marine origin. Within the heavily tectonized river valley, the original gypsum has nearly all been dissolved by upwelling mineral waters from the third aquifer, the "Upper Muschelkalk". This latter is a marine carbonate unit and the most important aquifer in this area for mineral waters of different chemical composition, depending on admixing of Gipskeuper groundwaters and deeper brines (Ufrecht, 1997). The mineral waters are artesically confined. Owing to extensive faulting, the mineral waters infiltrate locally into the oyerlying aquifers and the river.

Results and Discussion

The different surface waters, groundwaters, and mineral waters can be characterized and clearly differentiated on the basis of their O and H isotope composition (Fig. 1). Variations in the O and H isotope compositions can detect the locally variable influence of surface infiltration to the main aquifer. Furthermore, small-scale mixing processes between the different groups of waters can be recognized. In combination with the carbon isotope compositions of DIC the following influences can be distinguished within the Quarternary aquifer at the former gas production site: infiltration from shallow groundwaters derived from the adjacent steep hill along the western margin of the site; river infiltration along the eastern margin of the site, and local infiltration by artesically confined mineral waters in the northern part of the site.

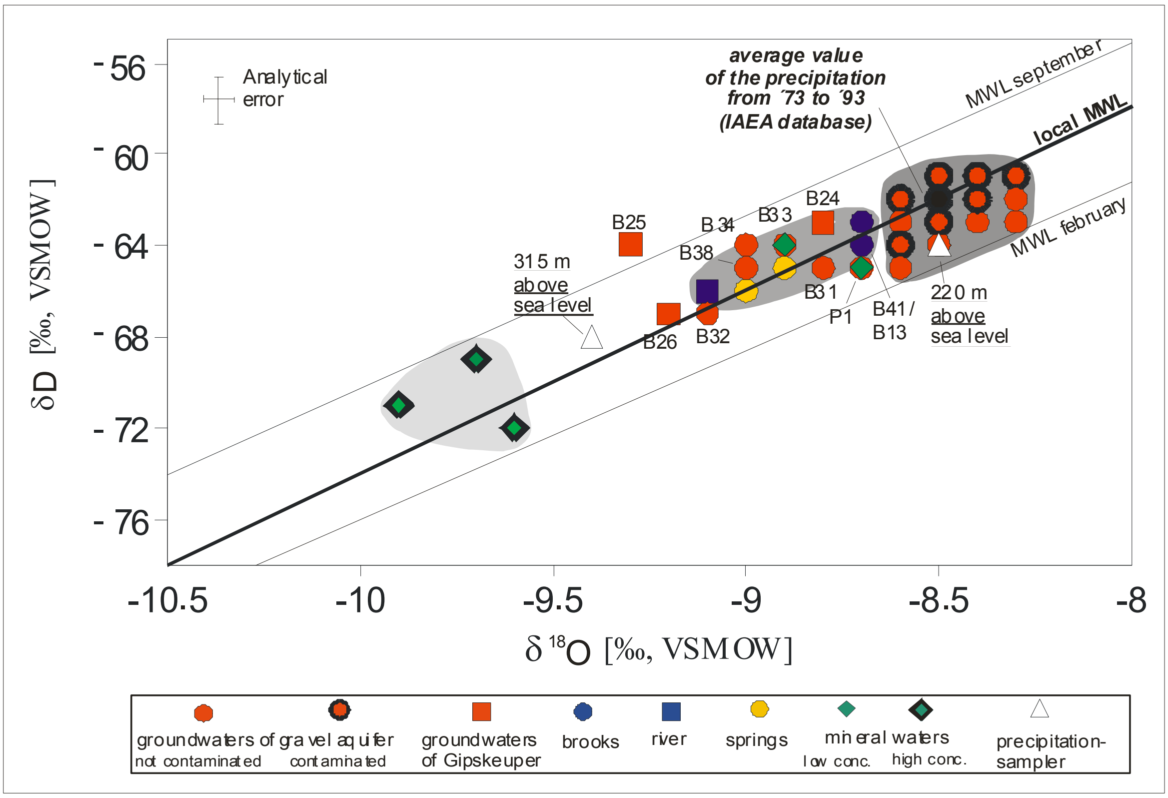

Fig. 1. Summary of the H- and O-isotope composition of the different ground- and surface waters sampled at the site.

Variable mixtures of these different waters within the gravel aquifers can be presented as mixing lines in terms of their stable isotope composition of O, H, and C_{DIC}, allowing for a calculation of the mixing proportions within individual boreholes. Quite surprisingly, the proportions of different waters in the boreholes vary considerably both in terms of space and time, depending on the flow regime of the adjacent Neckar river, the variable local recharge rates for surface waters, heterogeneities in flow rates owing to local differences in the permeability of the aquifer, and geologic as well as man-made structures penetrating the aquifer. A comparison of the isotopic compositions of waters sampled on a monthly basis over the course of two years indicates similar trends throughout each year, which reflects that there were no drastic changes in the weather pattern over the sampling period. However, large deviations in the isotopic compositions of the precipitation for individual months caused by particular precipitation events do allow for evaluation of reservoir effects and influences of man-made and geologic structures on the hydrology of the system. Seasonal variations in the isotopic composition of the different waters are related to seasonal variations in temperature and seasonably changing air masses in the recharge area. The magnitude of variation decreases significantly from precipitation via surface waters and down to groundwaters. The deep Gipskeuper groundwaters and mineral waters of the Muschelkalk aquifers show no relationship to actual precipitation owing to their distant recharge area and significantly longer flow paths, residence and mixing times within the aquifer. In the marginal areas of the site, groundwaters of the Quarternary gravel aquifer reflect the seasonal isotopic variations in precipitation but with a delay of about one month, indicating fairly rapid infiltration. Such seasonal variation is not recognizable in the central areas of the site owing to longer flow paths and residence times.

Interpretation of the carbon isotope compositions of the dissolved inorganic carbon (DIC) have been made in the context of different natural and anthropogenic carbon components making up the background (CO_2, carbonates, organic substances). The different components have significant differences in their carbon isotope composition: marine carbonates of the sediments as well as atmospheric and possible mantle-derived CO_2 are clearly enriched in ^{13}C compared to the natural and anthropogenic organic substances and the soil CO_2. The concentration and isotopic composition of DIC in most waters can be interpreted within the framework of the natural biogenic and geogenic carbon system (Fig. 2). DIC of small fluvial surface waters and local spring water sampled distant from anthropogenic carbon sources is predominantly influenced by soil CO_2, while DIC of the large river is, in addition, influenced by atmospheric CO_2. Seasonal variations of the carbon isotope composition and concentrations of DIC in different surface and groundwaters correlate with variable amounts of precipitation and runoff but generally do not correlate with the photosynthesis-respiration-cycle of natural plants. DIC in deep Gipskeuper and mineral aquifer waters is clearly dominated by marine carbonates, which make up these aquifers. In contrast to waters from uncontaminated sources, the DIC in the contaminated Quarternary aquifer is characterized by significant depletion of ^{13}C with values lower than those expected to be in equilibrium with natural soil CO_2. The remarkably low $\delta^{13}C_{DIC}$ values, especially in the polluted aquifers can not be explained by variations in the natural organic substances measured. Oxidative decomposition products from biodegradation of the organic pollutants are expected, however, to have low ^{13}C content and are likely to be responsible for the low δ^{13}C values of DIC in the Quarternary aquifer. The lowest δ^{13}C values and at the same time the highest DIC concentrations have been measured immediately *downstream* of the known pollution. Further downstream the DIC concentrations decrease and $\delta^{13}C_{DIC}$ values increase again, except for boreholes influenced by mineral waters, which have significantly higher DIC concentrations. Thus dilution and mixing effects can be clearly resolved. Generally low δ^{13}C values *upstream* of the former gas production site are likely to reflect regional anthropogenic contamination in the industrialized Neckar valley but not related to the contamination at the former gas production site.

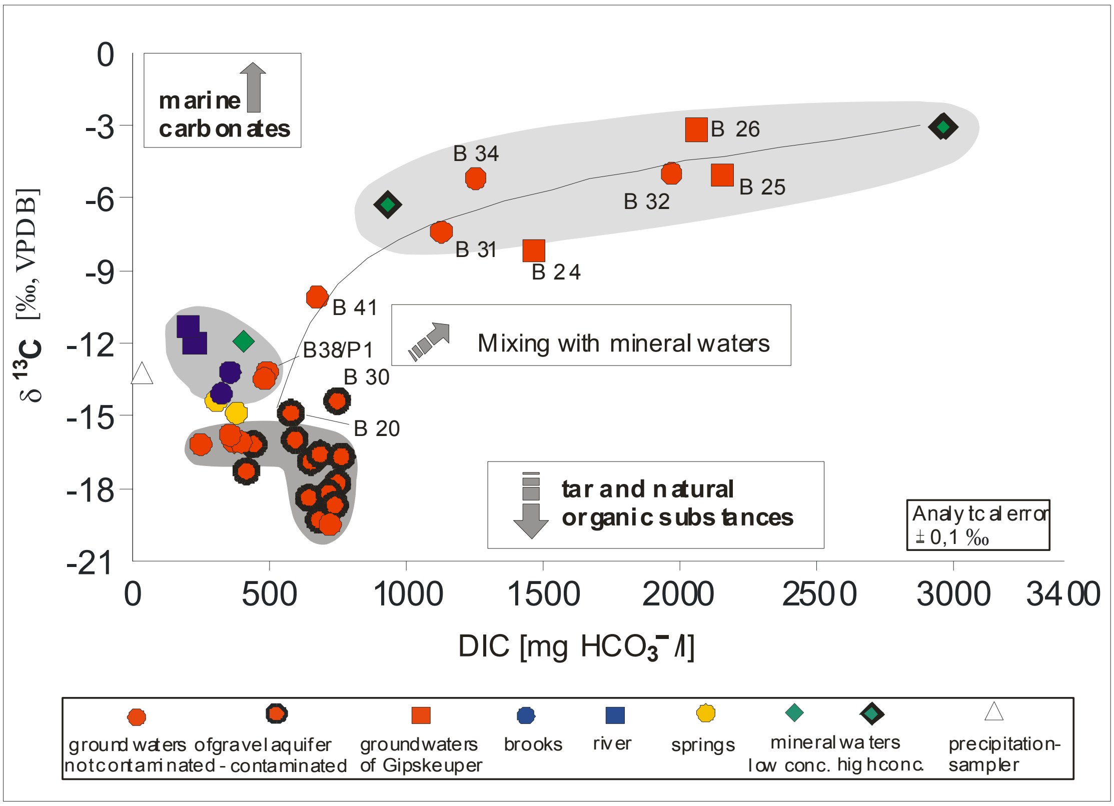

Fig. 2. C-isotope compositions versus bicarbonate ion concentrations of the different ground- and surface waters sampled at the site (from Angloher-Reichelt, 2001).

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Tracer tests with artificial tritium to derive hydraulic properties of constructed wetlands.

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Constructed wetlands technology (Kadlec and Knight, 1996) is a cost-effective and environmentally friendly method used world-wide to treat wastewaters of different origins. Efficiency of soluble pollutants removal is thus primarily related to the extent of contact between wastewaters and the reactive surfaces. Knowledge of hydraulic properties is therefore a prerequisite for studies of constructed wetlands functioning (Wachniew & Rozanski, 2002). Tracer technique is a valuable tool used to gain insight into wastewater flow phenomena in constructed wetlands. Residence time distribution (RTD) obtained as a breakthrough curve of a non-reactive tracer carries synthetic information on wetland hydraulic properties. Quantitative wetland characteristics are derived with help of an assumed mathematical model of wastewater flow.

This work summarizes tracer test performed with tritium and bromide (KBr) in a constructed wetland in Poland: horizontal subsurface-flow system with *Phragmites australis* in Nowa Slupia. Fig. 1 presents results of the test obtained for one of three parallel cells of the Nowa Slupia wetland. Solid line represents RTD fitted to experimental results on the basis of the Multi Flow Dispersion Model (Maloszewski et al., manuscript in preparation). Four peaks of the RTD presented on Fig. 1 reflect contribution of four components to the total flow through wetland cell. Three components are related to subsurface flow, the fourth component was identified as corresponding to surface flow. Hydraulic parameters (mean water travel times, water volumes, dispersion numbers) were derived for all flow components through each of wetland cells (see Table 1).

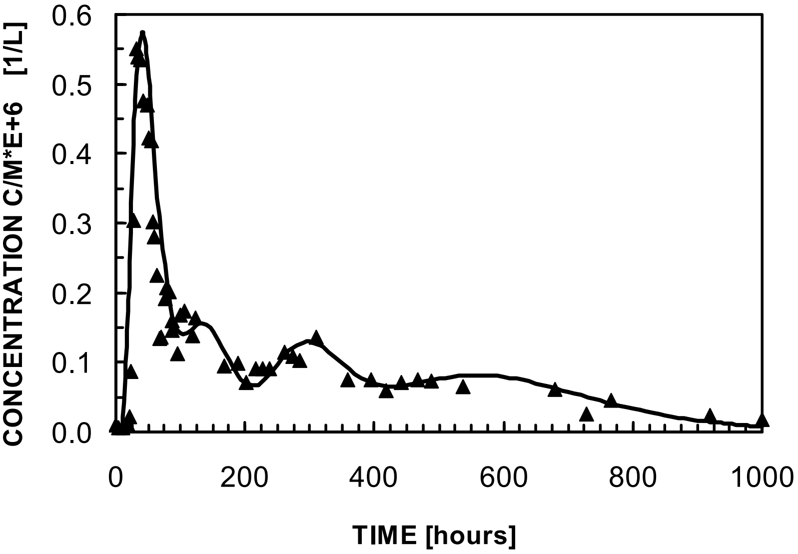

Fig. 1. Normalized output concentrations of tritium for one of cells of the Nowa Slupia wetland (triangles) and the fitted RTD (line).

Table 1. Model parameters fitted to the experimental RTDs for all flow components: mean water travel time - τ[h], dispersion parameter – P_D, relative contribution of the cell to the total flow – p.

		bromide			**tritium**		
		τ	P_D	p	τ	P_D	p
Cell 1	Flowpath 1	66	0.05	0.59	69	0.05	0.67
	Flowpath 2	130	0.03	0.21	132	0.03	0.19
	Flowpath 3	258	0.04	0.12	252	0.03	0.08
	Surface flow	650	0.04	0.08	560	0.04	0.06
Cell 2	Flowpath 1	95	0.16	0.35	93	0.13	0.42
	Flowpath 2	236	0.03	0.25	229	0.03	0.29
	Flowpath 3	488	0.02	0.17	433	0.01	0.10
	Surface flow	780	0.03	0.23	710	0.01	0.19
Cell 3	Flowpath 1	60	0.13	0.25	56	0.11	0.32
	Flowpath 2	156	0.03	0.15	156	0.03	0.15
	Flowpath 3	312	0.02	0.22	312	0.02	0.19
	Surface flow	650	0.03	0.38	650	0.04	0.33

Simultaneous use of two tracers allowed for comparison of their suitability for tracer tests in constructed wetlands. Differences in recoveries of tritium and bromide are related to evapotranspirative loss of tritium from the wetland.

Acknowledgements

This work was supported through the PRIMROSE project within the 5th Framework Program of Research, Technical Development and Demonstration of the European Union (EVK1-CT-2000-00065).

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Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Strontium isotope stratigraphy and oxygen and carbon isotopes in Upper Cretaceous sections of the Eastern Alps

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Several biostratigraphically well dated Upper Cretaceous sections in the Eastern Alps including the Cenomanian-Turonian, the Santonian-Campanian and the Campanian-Maastrichtian boundary interval, were investigated using $\delta^{18}O$, $\delta^{13}C$, and $^{87}Sr/^{86}Sr$ ratios. Within the section of the Rehkogelgraben near Gmunden (Ultrahelvetic Zone), the Cenomanian-Turonian boundary was investigated, including distinctive black shale horizons and the transition into red marls. The section starts with cyclic deposition of light grey, spotty limestones and medium grey marls where bioturbation is very common. The occurrence of nannofossils (nannofossil standard zone CC 10) indicates a Late Cenomanian age. Limestones display high abundances of planktonic microfossils, e.g. calcispheres and planktic foraminifera. 3 black shale layers are found within the overlying 1 m thick interval where the largest horizon is 16 cm thick. TOC values range around 5 % in this layer, carbonate contents are below 2%. Rock Eval analysis indicates predominant marine organic matter. Above this interval the base of nannofossil standard zone CC 11 is present. The Lower Turonian is characterized by a 2 m succession of white to light grey marly limestones with missing or thin marl intercalations. The marly limestones have high percentages of planktic foraminifera and their carbonate content varies between 65 and 92 %. $^{87}Sr/^{86}Sr$ isotope ratios have been increasingly used for stratigraphical correlations and a $^{87}Sr/^{86}Sr$ sea water standard curve has been established for the Phanerozoic. A first attempt to correlate biostratigraphy with strontium isotope stratigraphy was made in this section. First results show a slight but significant positive shift of $^{87}Sr/^{86}Sr$ isotope ratios compared to the standard curve. $\delta^{13}C$ shows a well known peak around the Cenomanian-Turonian boundary interval. $\delta^{18}O$ values give a rough estimate of mid-Cretaceous sea surface temperatures of about 28 – 30°C. This is fairly high compared to $\delta^{18}O$ values for the Santonian and Campanian of the same section which indicate sea surface temperatures between 20 and 24° C.

Ammonite, inoceramid, foraminiferal, and nannoplankton multistratigraphic data allow the recognition of the Santonian-Campanian-boundary interval in sections of the Gosau Group (Northern Calcareous Alps). In the Gosau area a fine-grained sandstone with late Santonian ammonites and inoceramids is overlain by a lower Campanian marly succession. Nannofossil data indicate the Santonian-Campanian-boundary in nannofossil standard zone CC 17. Strontium isotope data from the uppermost Santonian (brachipode shell) indicate an $^{87}Sr/^{86}Sr$ isotope ratio of 0.707468 ± 7. Sr isotope ratios of planktic foraminifera increase in the Lower Campanian up to 0.707590 ± 20.

In the Gosau Group of the Lattengebirge section near Berchtesgaden (southern Germany) a marly Santonian-Campanian boundary succession is present. Strontium isotope data from planktic foraminiferal tests can be compared to the standard strontium isotope curve and allow a detailed correlation of the Santonian – Campanian boundary to standard sections (0.707479 ± 5 for England, 0.707472 ± 12 for northern Germany). These values for the Santonian - Campanian boundary correspond to a level well below the first occurrence of *Globotruncanita elevata* in the Lattengebirge section. Strontium ratios increase up section to 0,707540 ± 10.

The Campanian-Maastrichtian boundary was investigated in Gams and Gosau (Northern Calcareous Alps). The position of the *Globotruncanita calcarata* planktic foraminifera Zone in regard to the standard definition of the lower boundary of the Maastrichtian in northern Germany was investigated. Our strontium isotope data for foraminiferal calcite of this zone (around 0.707670) confirm the results that this foraminiferal zone is of Late Campanian age and cannot be correlated to the Campanian-Maastrichtian boundary in northern Germany.

Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz | Bd. 8 | ISSN 1608-8166 | Isotope Workshop Volume | Graz 2004

Carbon isotope charactersitics of iron-oxidizing bacterial mats, Jackson Creec, Bloomington, IN, USA.

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We have investigated the isotopic composition of iron-rich microbial mat deposits that formed at the outflow of a freshwater spring along Jackson Creek in SE Bloomington/Indiana. The spring waters are of near neutral pH and contain dissolved iron (Fe^{2+}) that is derived from oxidation of diagenetic pyrite in the Mississippian Borden Formation. Although one might assume that iron deposition is simply due to oxidation to Fe^{3+} and subsequent precipitation of iron hydroxides, iron deposition is directly correlated with a thriving community of iron bacteria. The bacteria form loaf-shaped and bulbous buildups up to 20cm diameter, as well as undulose mats of a few cm thickness that cover the creek bed. The sheath forming bacterium *Leptothrix* dominates, but spiral stalks of *Gallionella* are commonly present, as well as other currently unidentified microbes. Microbial growth

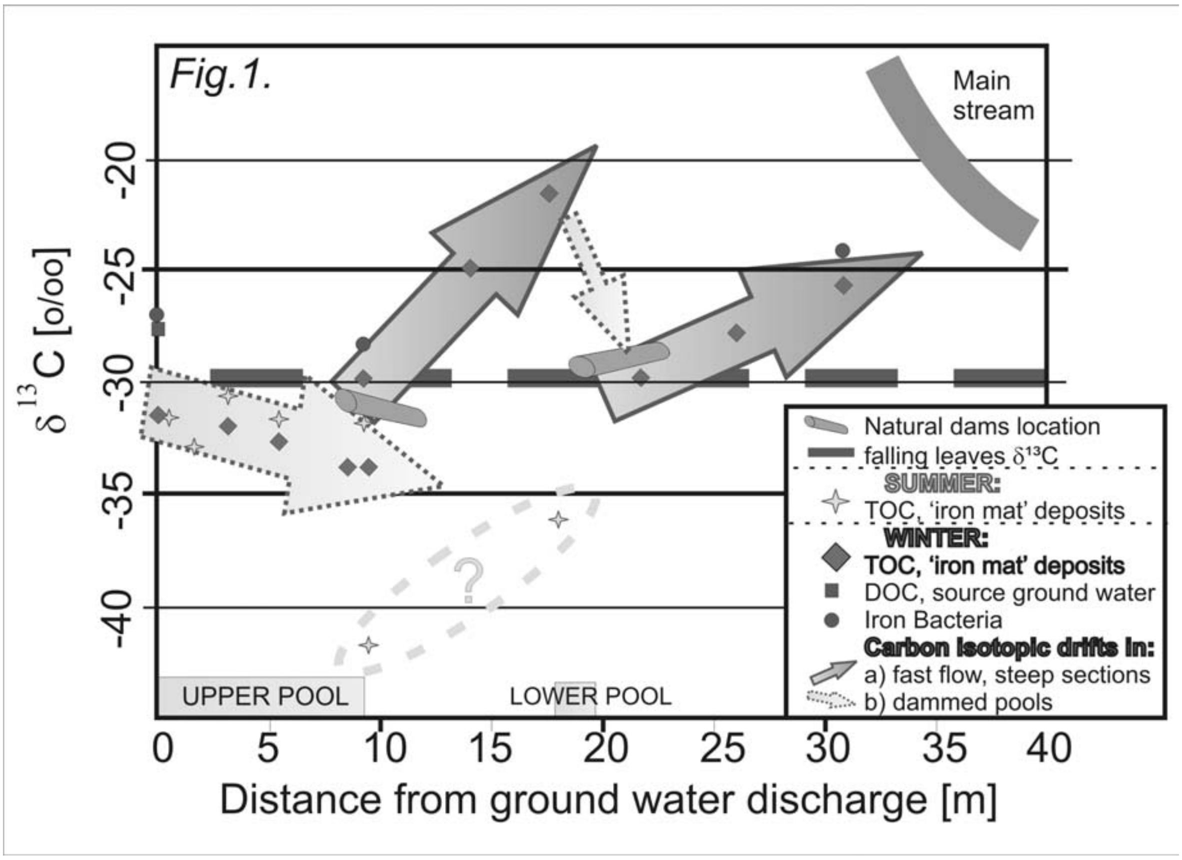

Fig.1. Changes in $\delta^{13}C$ values of organic carbon from microbial mats along the creek. Additionally $\delta^{13}C$ values of DOC in the spring, decaying leaves and of bacteria are shown.

forms are fragile and are flushed out entirely during peak runoff associated with heavy rains. However, regrowth of microbial mats is vigorous and full mat coverage can be achieved within a weeks of time.

Chemoheterotrophs like *Leptothrix* are not considered true iron oxidizers, and precipitation of iron is considered spontaneous without providing energy to the organism. But some authors suggest that *Gallionella* (chemoatuotroph) may gain energy from the process and in addition gets carbon for building its cells from CO_2 as shown in the reaction:

$$4Fe^{++} + HCO_3^- + 10H_2O \rightarrow 4Fe(OH)_3 + [CH_2O] + 7H^+$$

However, the apparent independence of the mat formers in our study from seasonal variations in organic matter supply (their growth rate shows no change with seasonal fluctuations), as well as their occurrence only near a source of iron-rich (12.5 ppm Fe) waters, seems to suggest that iron availability confers a tangible benefit. This benefit could be energy gain or alternatively a reduction of ambient pO2 because *Leptothrix and Gallionella are* considered microaerophilic. This open question may be answered in the near future through an ongoing examination of iron isotopes.

Carbon isotope data from terrestrial iron bacteria mats show fractionation relative to the composition of the likely source material. Also we have observed very high ability of these bacterial colonies to drift its carbon isotopic values in order of 1‰ per 1 meter down the creek. Observed dirfts occure in both directions and the direction depends on flow regime and availability of carbon supply. On fig.1 one can notice that in dammed pools in the creek isotopic shifts toward more negative values are observed due to organic matter build up and recycling. Contrary in the fast flow sections the situation of limited nutrient supply occurs as the water flows down, thus the remaining portion of DOC flowing down the creek gets heavier and heavier as bacteria preferentially uptake isotopically lighter nutrients. These observations were confirmed by the relationship of TOC content in the mats and its carbon isotopic composition. When there is plenty of DOC we observe higher TOC content in colonies and more negative $\delta^{13}C$ values. Again, contrary in zones with regime of limited DOC supply we observe lower TOC content in the colonies and less negative $\delta^{13}C$ (fig.2).

Thus, carbon isotope fractionation may be used as a potential biosignature for identifying microbial involvement in fossil equivalents. Microbial recycling of initially produced organic compounds may impart further fractionation, and can produce broad and perhaps erratic appearing C-isotope signatures. Also primitivness and self-sufficiency as well-as well compounds on which these organism rely (especially *Gallionella*) makes them a good candidate for extraterrestrial forms of live that could have been evolved in similar environments to the Early Earth, like with high probability Mars was 3.5 billion years ago.

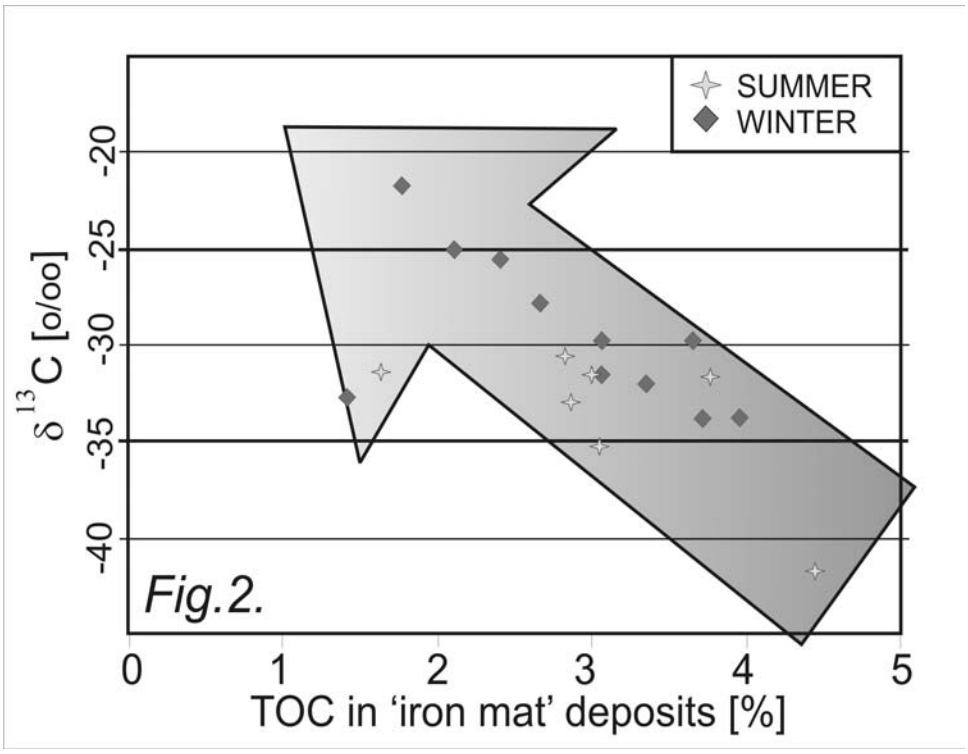

Fig.2. Inversely proportional relationship between TOC abundance in the mat material and its δ^{13}C values.

Index of names

The financal support of these institutions and companies is gratefully acknowledged:

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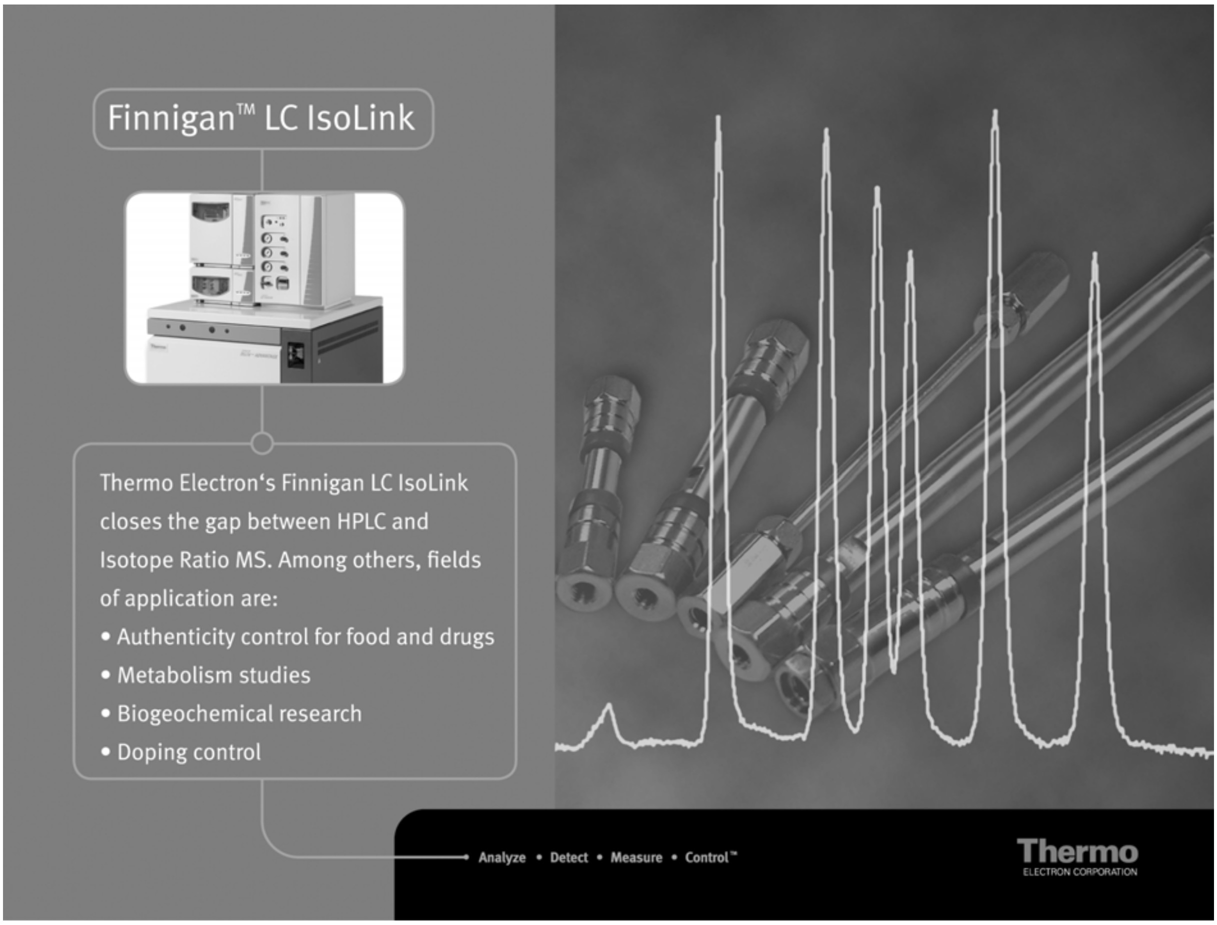

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