



4 th Mini Conference on
Noble Gases in the Hydrosphere
and Natural Gas Reservoirs



<http://minoga.gfz-potsdam.de>

Conference Proceedings

4th Mini Conference on Noble Gases in the Hydrosphere and Natural Gas Reservoirs

The conference is held from February, 28th to March 2nd, 2007
at the GFZ Potsdam, Germany's National Research Centre for Geosciences
at Potsdam, in the outskirts of Berlin.

Deutsche
Forschungsgemeinschaft
DFG

The Mini Conference will be financially supported by the Deutsche
Forschungsgemeinschaft (DFG), the German Science Foundation.

GeoForschungsZentrum Potsdam in the Helmholtz Association of German Research Centres



Convener

Dr. Johanna Lippmann-Pipke
Inorganic and Isotope Geochemistry
GeoForschungsZentrum Potsdam
Telegrafenberg B323
14773 Potsdam, Germany

Now at:

Institute for Interdisciplinary Isotope Research
IIF Leipzig
Georadiochemistry, Head
Permoserstr. 15
04318 Leipzig, Germany
lippmann@iif-leipzig.de
www.iif-leipzig.de

Prof. Dr. Werner Aeschbach-Hertig
Institute for Environmental Physics
Groundwater and Paleoclimate, Head
Heidelberg University
INF229
69120 Heidelberg, Germany
aeschbach@iup.uni-heidelberg.de
<http://www.iup.uni-heidelberg.de>

Bibliographical Data:

J. Lippmann-Pipke and W. Aeschbach-Hertig, (eds.) (2007): 4th Mini Conference on Noble Gases in the Hydrosphere and in Natural Gas Reservoirs. Abstract Volume. GFZ Potsdam, Germany, 28.02.-02.03.2007. doi 10.2312/GFZ.mga.050

Conference Proceedings

4th Mini Conference on Noble Gases in the Hydrosphere and Natural Gas Reservoirs

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at the GFZ Potsdam, Germany's National Research Centre for Geosciences

Editorial

After the previous meetings in Lamont, Columbia University, NY (1992), in Paris, France (1994) and at EAWAG, Kastanienbaum, Switzerland (1997) on similar topics, we have the pleasure to announce the 4th Mini Conference on “Noble Gases in the Hydrosphere and Natural Gas Reservoirs” at the GFZ Potsdam, Germany's National Research Centre for Geosciences in the city of Potsdam, in the outskirts of Berlin, Germany.

These *Conference Proceedings* enclose 49 abstracts that are being presented during this three-day, single session conference.

- Session 1: Applications of noble gases in hydrology
- Session 2: Advances in data evaluation and interpretation
- Session 3: Noble gases in natural gas reservoirs
- Session 4: Applications of noble gases in *new* archives
- Session 5: Technical advances in noble gas analysis
- Session 6: Combining other tracers with noble gases

The general concept of this mini conference is to provide the participants with enough time for spontaneous contributions and discussions after each talk, during the poster sessions, the ice-breaker-party, lunch and coffee breaks. One prerequisite for this concept to be successful was to limit the number of participants to about 50. Then, we all may profit from the natural advantage of a mini conference: its small size and informal atmosphere.

Lucky-us! There was no need to reject any interested participant. Though we initially advertised this conference only among a smaller group of scientists, obviously the news spread wide enough that, even as we finally posted on the NOBLE-GAS-NETWORK, we were not swamped: A total of 59 participants from 13 countries have finally registered: Scientists from Australia, Austria, Canada, Estonia, France, Netherlands, Germany, Italy, Japan, Poland, Switzerland, UK and the USA are well representing the "noble gases in the environment" community.

Of course we hope that this meeting will be as productive as its precursors, and that the concept of such focused mini conferences in our field will regain momentum, such that the tradition will soon be continued.

The homepage of the conference is – among other things - the platform from which electronic versions of the schedule, all the individual abstracts, these Conference Proceedings and a group photo can be downloaded: <http://www.minoga.gfz-potsdam.de>

We would like to thank the Deutsche Forschungsgemeinschaft (DFG, German Science Foundation), as well as the GFZ Potsdam for financial, administrative and logistic support.

Potsdam, 28th of February, 2007

Johanna Lippmann-Pipke and
Werner Aeschbach-Hertig
Conveners

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Scientific Program

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Session 1:

Applications of noble gases in hydrology

Established methods in noble gas hydrology (^3H - ^3He , noble gas thermometry, ^{85}Kr , etc.), recent field studies (water recharge management etc.)

Excess Helium in the Edwards Aquifer

Andrew G Hunt¹ and Gary P. Landis¹

¹ U.S. Geological Survey, Noble Gas Laboratory, Denver, Colorado, USA

Noble gas and other geochemistry of the fresh and saline water zones and transitional interface within the Edwards aquifer in south central Texas reveal a complex multi-sourced ground water history. Noble gas concentrations in the freshwater zone are characteristic of air equilibrated, tritium-bearing waters with minor amounts of excess air. Samples collected from the down-dip saline zone are tritium-dead with noble gas concentrations indicating mixing between air saturated waters and multiple end member hydrocarbon reservoirs. The concentration of dissolved helium in the freshwater/ saline water transition zone increases to levels almost 3000 times that of fresh water solubility. The isotopic composition of this excess helium indicates three separate end members, two from the Edwards saline zone and one from the fresh ground waters of the underlying Trinity aquifer. The two end members from the saline zone waters have distinct end member compositions of 0.14 and 0.22 R/R_A while freshwaters associated with subsurface discharge from the Trinity aquifer are on the order of 0.02 R/R_A. The elevated helium concentrations and high isotopic ratios in saline waters require an accumulation from a regional flux of ³He-rich helium into the stagnant, saline ground waters of the aquifer. No relation is observed between helium isotopic compositions of the aquifer rocks and the saline waters, as determined from released helium compositions from carbonate rocks and 72-81 Ma hypabyssal basaltic intrusions (alkali basalts, basanites and nephelinites). The carbonate rocks that comprise a majority of the aquifer have low concentrations of helium coupled with relatively low helium isotopic ratios (~ 0.07 R/R_A), while the

vitreous to aphanitic basaltic intrusions (including olivine phenocrysts and xenoliths with fluid/gas inclusions) have relatively high helium concentrations with isotopic ratios closer to that of radiogenic production values (< 0.05 R/R_A). The helium composition derived from the rocks that comprise the intrusions is that of the local upper mantle to lower crust transition at depth in the region of partial melting and mafic magma petrogenesis. Due to a lack of large quantities of ³He within this deep reservoir, the elevated amounts of ³He observed in the saline zone waters cannot be attributed to a broad, regional flux of mantle helium. The unique helium isotopic compositions in the saline waters must have accumulated prior to the saline waters migrating into the Edwards aquifer, and implies that the saline waters, may originate from regional fluid migration coupled with hydrocarbon entrapment through the area.

Byproducts of ³H-³He-Dating: use of radiogenic ⁴He to demonstrate mixing.

J.Sültenfuß¹

¹Institute of Environmental Physics, University of Bremen, Germany

A large set of groundwater samples from different sites in Northern Germany taken from monitoring wells in glacial sands is analysed for tritium, helium isotopes and neon. As a residue of the ³H-³He dating method Ne and ⁴He are used to derive mixing properties.

Low level tritium analysis is used to identify water infiltrated significantly before 1950. The low detection limit allows to separate between infiltration periods differing by 10s of year between 1950 and 1900.

Helium isotopes confirm a radiogenic ³He/⁴He-ratio of $2 \cdot 10^{-8}$. From this it follows that a clear separation of tritogenic ³He is possible.

Surprisingly, for samples with tritium concentration below 0.2 TU, no tritogenic ³He remaining from natural tritium could be found. Presuming no degassing, expected concentration for tritogenic ³He should be about 5 TU in Germany.

Fig.1 compares derived ³H-³He ages and concentrations of the sum of tritium and ³He of 120 samples with the tritium concentration in precipitation, labelled by their concentration of radiogenic ⁴He.

Radiogenic ⁴He is used to identify mixing processes of younger waters with old and tritium-free water. Samples with ages less than 20 years follow basically the presumed input. Therefore a significant admixture of tritium-free water can be excluded. This also indicates small age spectra.

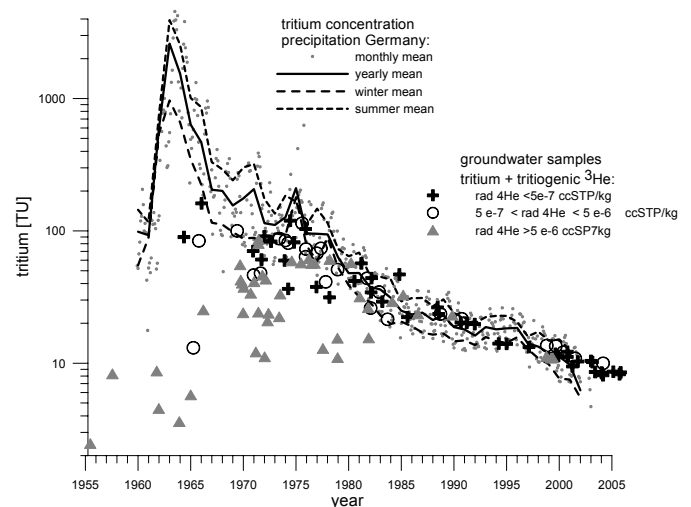


Fig. 1: 'stable tritium' vs tritium in precipitation

Under special conditions excess air derived from Ne concentrations can be used as water mass tracer, identifying mixing portion. Fig.2 displays Ne excess for 6 monitoring wells around the production well 3.

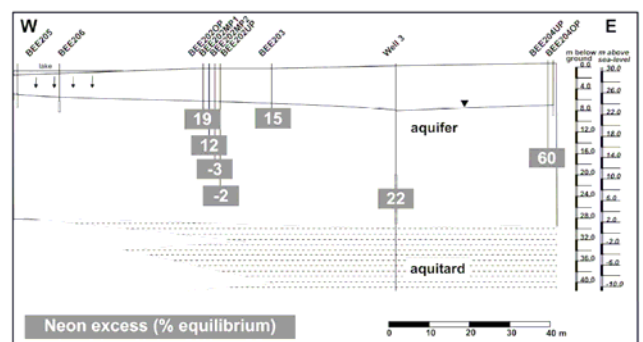


Fig.2: Excess air around a production well.

Buffering of Recharge Temperature Response to Climate Change in an Intermountain Basin, New Mexico, USA

A. H. Manning¹

¹ *United States Geological Survey, Denver, Colorado, USA*

Noble gas recharge temperatures and radiocarbon ages were determined for ground-water samples collected from the Española Basin located in the Rio Grande rift zone in northern New Mexico, USA. Geochemical mass balance modeling was performed using NETPATH [1] to derive radiocarbon age corrections. Uncertainty in the corrected radiocarbon ages was assessed by varying input parameters within reasonable limits and observing the resulting range of age corrections. Age corrections are generally <5,000 yr. Noble gas recharge temperatures were derived from measured concentrations of Ne, Ar, Kr, Xe, and N₂ using a chi-squared minimization method. Previous paleoclimate studies employing noble gas recharge temperatures performed in other aquifers in the south-central and southwestern U.S. show an increase in recharge temperature of 5-6°C occurring between 15,000 and 5,000 yr BP [2,3,4]. Recharge temperatures from the Española Basin show a similar increase of 4-5°C, but this increase occurs around 25,000 yr BP; recharge temperatures remain nearly unchanged (mean of 11.0°C) from 25,000 yr BP to the present. N₂-Ar recharge temperature determinations from the Middle Rio Grande Basin, the adjacent basin to the south, also display this trend [5]. It is possible that mean annual air temperature in the Española Basin increased around 25,000 yr BP instead of around 10,000 yr BP as in most other parts of the world. However, a more likely explanation is that the mean annual air temperature did increase around 10,000 yr BP in the Española Basin, but the recharge temperatures do not reflect this change because they were essentially buffered by

an accompanying increase in recharge elevation. In the current climate, recharge mainly occurs in the mountains adjacent to the basin (where precipitation is significantly greater than on the basin floor) and as focused infiltration along streams sourced by mountain precipitation. Little distributed recharge occurs on the basin floor because conditions are too arid. However, in addition to air temperatures being lower, precipitation was significantly greater in the western U.S. from 25,000 to 10,000 yr BP [6]. These conditions could have resulted in the ET threshold being exceeded on the basin floor and the occurrence of distributed recharge. In contrast, these conditions probably did not result in significantly more recharge in the mountains, but instead simply caused increased runoff (and thus more focused recharge on the basin floor) due to the relatively low permeability of the fractured rock composing the mountain block. Therefore, the mean recharge elevation for the basin could have been substantially lower than today under these climate conditions. Current water table temperatures throughout most of the basin (the Pajarito Plateau excepted) are 13-17°C. A reduction in the mean annual air temperature of 5°C would result in distributed basin floor recharge having a recharge temperature of 8-12°C, consistent with observed recharge temperatures for samples with ages of 25,000 to 10,000 yr (mean of 10.5°C). Conditions in the Española Basin prior to 25,000 yr BP may have been drier, but not warmer, than from 25,000 to 10,000 yr BP. The mean recharge elevation for the basin prior to 25,000 yr BP may thus have been similar to that today, resulting in the recharge tem-

peratures expected (mean of 6.7°C) given mean annual air temperatures 5°C cooler than today. An increase in precipitation from 30,000 to 25,000 yr BP would be consistent with records of alpine glacial advances in the nearby San Juan Mountains and of rising lake levels throughout the western U.S. during the same time period [6,7]. In short, recharge temperatures and radiocarbon ages from the Española Basin suggest: (1) recharge temperatures in arid and semi-arid intermountain basins may be essentially buffered against decreases caused by cooler climate conditions if the cooler air temperatures are accompanied by increased precipitation (as is commonly the case) and resulting lower recharge elevations; and (2) changes in recharge elevation due to changes in precipitation must be carefully considered along with changes in mean annual air temperature in the interpretation of recharge temperature data in paleoclimate studies.

Acknowledgments

This work was funded in part by Los Alamos National Laboratory and the City of Santa Fe, New Mexico.

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Noble gas paleo-temperatures in the North China Plain

Andreas M. Kreuzer¹, Christoph von Rohden¹, Werner Aeschbach-Hertig¹

¹*Institut für Umweltphysik, Universität Heidelberg*

Abstract

Noble gas temperatures (NGTs), stable isotope ratios and ¹⁴C-ages from recent and old groundwater in the North China Plain (NCP) are used to reconstruct a paleoclimate record. This is the first NGT record from East Asia containing clear holocene and pleistocene samples. Preliminary results indicate a glacial cooling of about 5°C.

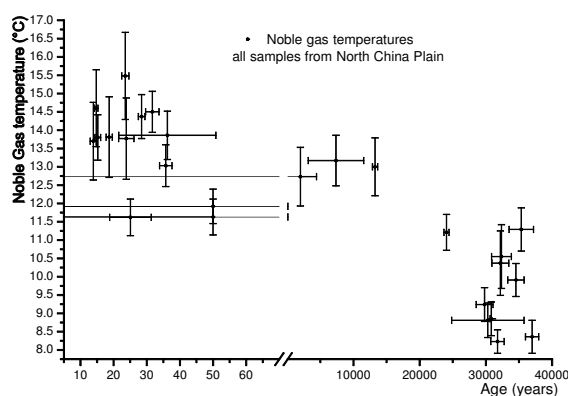


Figure 1: The figure shows the noble gas temperatures for the samples from 2004 and 2005. The warm temperatures of about 14°C in the modern samples correspond to the local annual soil temperatures and are slightly higher than the mean annual air temperature. The coldest late pleistocene samples have a temperature of about 9°C which would indicate a 5 K cooling for the NCP during the last glacial. Dating was done with ³H-³He for modern samples and with ¹⁴C for paleosamples.

Methods

During two sampling campaigns in two consecutive years 52 wells were sampled for noble gases, stable isotopes, SF₆, ¹⁴C and ³H. The samples were taken from currently used irrigation wells and water-supply-wells along a transect across the North China Plain from West to East. The noble gases were measured at the ETH in Zurich (Switzerland). Stable isotopes and Tritium were measured at the Institute of Environmental Physics

at the University of Heidelberg. ¹⁴C-Samples were extracted in Heidelberg and measured at the AMS Radiocarbon Lab, ETH Zurich (Switzerland). Noble gas temperature calculation was done by the noble90-Program. ¹⁴C-age reconstruction was done by a multimodel intercomparison procedure.

Results

More than 60% of all samples were younger than 50 years and already show anthropogenic influence, only three samples were from the early holocene. 20% of all samples were from the last glacial period with ¹⁴C-ages dating from 25-35 ka. The rest was mainly influenced by a deep fault-zone or gave a bad fit for NGT. The observed difference in NGT is used to interpret the $\delta^{18}\text{O}$ -signal. The value for T- $\delta^{18}\text{O}$ -slope for modern and paleogroundwater is calculated to be $0.25 \pm 0.04\text{‰}/^\circ\text{C}$ and $0.17 \pm 0.04\text{‰}/^\circ\text{C}$ respectively. While a large shift in $\delta^{18}\text{O}$ occurs from a change in the strength of the monsoon. A strong Asian monsoon leads to humid conditions in the North China Plain and lowers the $\delta^{18}\text{O}$ -signal independent of the temperature-effect by $1.5 \pm 0.2\text{‰}$.

Acknowledgments

This work is financially supported by the DFG (DFG grant AE 93/1) and by the National Natural Science Foundation of China (NSFC grant No. 40472125)

Laboratory and field experiments on the formation of excess air in groundwater

L. Palcsu¹, W. Aeschbach-Hertig¹, M. Kopf¹, E. Zechner²

¹ *Institute of Environmental Physics, University of Heidelberg, Germany*

² *Environmental Geology, University of Basel, Switzerland*

Excess air is a contribution to the gases dissolved in groundwater in addition to the solubility equilibrium component [1], formed by partial or total dissolution of entrapped air between the soil particles in the unsaturated zone during water level rises [2].

Although, excess air formation has been observed for more than two decades, so far only a few studies investigated the process in detail [3–5]. One of the main goals of this project is to investigate the mechanisms that control the excess air formation. We examine the formation of excess air under field and laboratory conditions using all five noble gases. In laboratory experiments with plexiglas columns filled with different types of sand, we investigate how the excess air amount and composition depend on the hydrostatic pressure as well as the size distribution of the sand and the entrapped air bubbles. In field experiments we study the relationship between excess air and water level fluctuations.

Laboratory experiments

As a first step, we want to check that the excess air component as well as the fractionation indeed depends on the hydrostatic pressure. In fact, using the closed-system equilibration model [2] to describe the measured noble gas values one should be able to determine the entrapped air volume in the inverse fitting of the noble gas concentrations. We used two different types of sand, a coarse and a fine one. Their grain size ranged between 0.2–1.0 and 0.1–0.2

mm, respectively. Two columns had been filled with sand and air equilibrated water, and after 48 hours samples were taken from different depth.

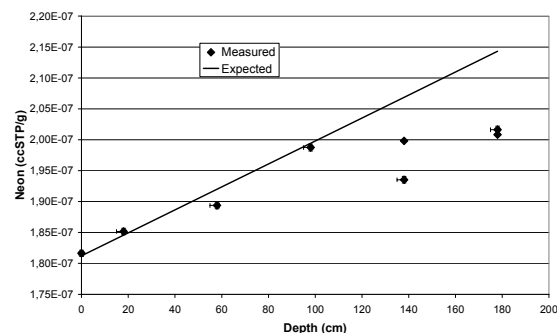


Figure 1. Neon values from different depths and the expected values according to the hydrostatic pressure in case of the coarse sand (duplicates for higher depths).

In Fig. 1. one can observe that the excess neon amount increases with depth. So do the other noble gases (not shown). However, at higher depths, the values deviate from the expected values, which needs an explanation. These and other processes will be investigated in detail soon.

Field experiments

We have selected an appropriate study site where we can examine excess air formation under natural conditions. At this site (alluvial plain of Wiese River, Basel, Switzerland) a few small fields are flooded artificially with filtered river water from the Rhine, in order that the biologically active surface of the soil particles further purifies the water for drinking purposes. Each flooding takes 10 days, then the fields are

let to go dry (for 20 days), thus the groundwater level is fluctuating regularly. That is why it seemed to be a good opportunity to take water samples in order to find a correlation between the excess air amount and the water level increases.

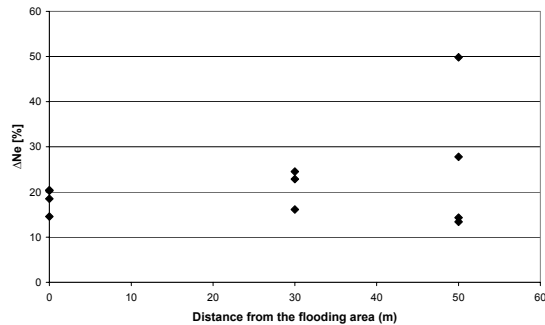


Figure 1. Neon excesses along the groundwater flow line from the flooded field

During a whole flooding cycle we took several samples from different monitoring wells along the flow path of the groundwater from the flooded field. Distinguishable amounts of excess air have been found in all of the groundwater samples. Even though the water level increase did not exceed 1 m, thus neither the hydrostatic pressure exceeded 0.1 atm, 15 to 30 % of neon excess were found in most of the samples (Fig. 2).

Taking into account that the flood water has nearly no excess, these high excess air components cannot be explained solely by pressure increase in the entrapped air. Oxygen depletion due to biological processes might play a role, when O_2 is consumed, then all of the noble gas partial pressures are elevated [6]. At that elevation (270 m a.s.l.) and at 18 °C, the saturated dissolved O_2 is about 8.6 mg/l, instead, we found significantly lower quantities in our water samples. The dissolved oxygen in the water samples were varying between 1.6 and 5.2 mg/l. If the oxygen is vanishing in the entrapped air, increasing the partial pressure of all other gases, this process could be responsible to create additional 14–21 % Ne excess.

The field experiments are going on, more detailed evaluations will be done this year.

Acknowledgments

This project is supported by the Marie Curie Intra-European Fellowships program (reference number: 009562).

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⁴He and Noble Gases in Buried Valley Aquifers: Dating, Recharge, and Complications

S. J. Van der Hoven

*Department of Geography-Geology
Illinois State University
Normal, Illinois, USA*

Introduction

⁴He used primarily as a tool in large basin with old groundwater (>10 kya). My interests are in applying it as a tool in younger groundwater (10s-1000s years old). This may be most applicable to glacial aquifers where recently eroded sediments may be releasing stored ⁴He at rates up to several orders of magnitude higher than production rates based on U/Th concentrations [1][2].

My research has focused on the Mahomet Aquifer, a buried valley aquifer in central Illinois, USA, and has focused on identifying patterns of ⁴He accumulation along the main flow path, measuring the ⁴He release rate from aquifer sediments, identifying the mechanism for observed gas loss in parts of the aquifer and its effects on ⁴He accumulation, and using noble gas ratios to identify recharge areas for the aquifer.

The goals of this research are to constrain the internal and external fluxes of ⁴He, establish ⁴He as a stand-alone dating technique for young groundwater, and to incorporate ⁴He and noble gases in numerical models of this aquifer and other aquifers with similar characteristics.

Sources of ⁴He

Accumulation ⁴He in groundwater due to in situ production of ⁴He is most often calculated based on the U/Th concentration of sediments [3] or by modeling diffusive release [4]. However, these techniques are not universally applicable. Numerous studies have shown that the accumulation rate can be significantly different than the

U/Th production rate, and to use diffusion modeling the sediment grain size and geologic history must be well known. Both these techniques use mg samples sizes that may not reflect geologic heterogeneity.

A technique that may be applicable to calculating in situ production in all geologic settings is direct measurement of sediment release rates. This technique involves placing about 100 g of sediment in a container under vacuum, and measuring the rate of ⁴He release as a function of temperature, and then converting to the accumulation rate in groundwater at the in situ temperature. While this technique is time consuming (4-6 months), it does not have the disadvantages of the U/Th and diffusion methods.

A limited number of release rate experiments have been performed on aquifer sediments. These experiments indicate that the ⁴He release rate is approximately equal for sediments from different parts of the aquifer. Additional release rate experiments are currently being performed.

In addition to in situ production, the patterns of ⁴He accumulation in the Mahomet Aquifer indicate that diffusion/advection from the underlying bedrock is a source of ⁴He to parts of the aquifer. There is currently no information on ⁴He concentrations in the underlying bedrock.

Interactions with CH₄ Gas Pockets

Groundwater in large parts of the aquifer has lost atmospheric gases as indicated by negative Δ Ne values. The mechanism of gas loss appears to be interaction with

pockets of biogenic CH₄ (locally known as drift gas) that are common in the fine-grained units overlying the aquifer. As groundwater migrates vertically through these confining units, it interacts with the drift gas and loses/gains gas in solution.

The drift gas can consist of up to 50% N₂, indicating that the source of drift gas is gases in groundwater. The interaction between groundwater and drift gas pockets appears to be an equilibrium process, as indicated by similarity in noble gas ratios of groundwater and calculated theoretical equilibrium ratios based on noble gases in drift gas samples [5]. It is still an open question as to whether ⁴He values can be “corrected” for this interaction before water enters the underlying aquifer.

Implications for Dating and Recharge

In parts of the aquifer where the flux of ⁴He from the underlying bedrock appears to be low, ⁴He maybe useful as a dating technique. The release rate experiments indicate that measurable ⁴He accumulates in groundwater in <100 years. The ⁴He ages calculated using release rates are comparable to ¹⁴C ages from the aquifer. In parts of the aquifer where the bedrock ⁴He flux is higher, dating is most likely not possible.

While the gas loss due to interactions with drift gas cause complications for ⁴He, the noble gas ratios provide quantitative information on aquifer recharge. Groundwater in the main recharge area of the aquifer has not lost gases (positive ΔNe values), and does not appear to interact with drift gas as it migrates vertically through the sediments overlying the aquifer. With increasing distance away from the main recharge area, the ΔNe values decrease.

The decrease in ΔNe values is conceptualized as groundwater recharging past drift gas and mixing with undegassed groundwater already in the aquifer. Using this conceptual model, calculations can be performed where air saturated water is mixed with water in equilibrium with drift gas. These calculations indicate that groundwater with negative ΔNe values is >50 water

that has equilibrated with drift gas. This contradicts the current consensus that the confining units provide little recharge to the aquifer.

Future research includes additional release rate experiments, quantifying the bedrock ⁴He flux, and applying these techniques to other bedrock aquifers.

Acknowledgments

Funding for this research was provided by the Illinois State Geological Survey, the Illinois Board of Higher Education, and Illinois State University. Graduate students Erik Wright, David Carstens, and Tim Sickbert were involved in sampling, analysis, and interpretation of these data. Drift gas samples were provided by Dennis Coleman.

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Session 2:

Advances in data evaluation and interpretation

Methods to calculate groundwater ages and noble gas temperatures, excess air models, degassing-mixing models, groundwater transport models, etc.

Lessons Learned from Two Thousand Tritium-Helium Groundwater Ages in California, USA

Jean E. Moran¹, G. Bryant Hudson², Bradley D. Cey³, and Michael J. Singleton¹

¹Lawrence Livermore National Laboratory, L-231, 7000 East Ave., Livermore, CA 94550 USA

²Lawrence Livermore National Laboratory, current address: Blackjack Trail, Norman, OK

³University of Texas at Austin, Austin, TX

Study Design

A state-wide, comprehensive study of groundwater contamination vulnerability in California, USA uses ³H-³He groundwater age to assess the relative probability that drinking water aquifers will become contaminated with anthropogenic pollutants. Nearly all of the wells included in the study are public drinking water supply wells. There are ~16,000 public supply wells in California; wells sampled for this study are a subset (nearly 2000 to date) from large metropolitan areas (Los Angeles, Orange County, San Jose, and Sacramento), as well as several smaller population centers and rural areas that may rely entirely on groundwater for drinking water supply. The large data set for dissolved noble gases and tritium-helium age allows basin-wide and regional analysis of groundwater age, excess air, and recharge temperature not possible in typical studies with a small number of wells or low sample density.

Results

Forty percent of wells have tritium concentrations less than 4 pCi/L, indicating that at least 80% of the water produced recharged more than 50 years ago. In basins where focused artificial recharge dominates the flow field, relative groundwater ages are good predictors of the probability for wells to be contaminated with anthropogenic compounds (figure 1). Wells producing relatively young groundwater invariably are affected by low-level contaminants,

while tritium-dead water is nearly always free of the same compounds. Analysis of a large number of spatially distributed samples is necessary to delineate the flow field and identify recharge areas using relative ages.

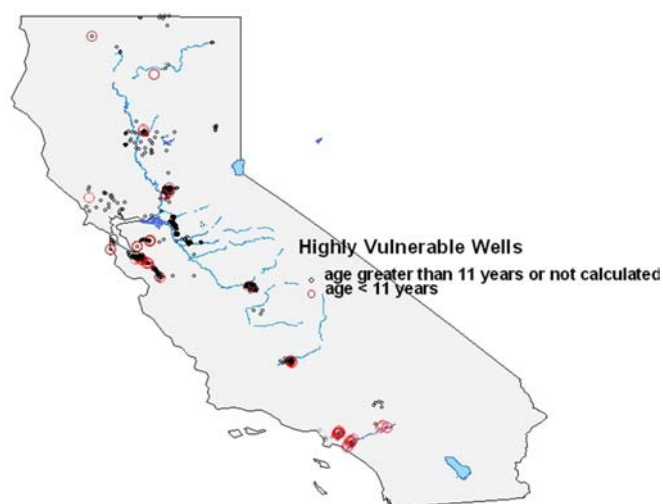


Figure 1. Map of California showing areas where tritium-helium age data has been collected and wells with ages <11 years.

Ten percent of wells have a mantle helium component. In mixed samples containing tritium, mantle helium is recognized as having more ³He than can be supported by the tritium observed. Mantle helium is widespread in wells from volcanic provinces in northern California, but occurs rarely, along certain tectonic features, elsewhere in the state.

Comparing the calculated groundwater age and (decay corrected) measured tritium reveals useful information about the

groundwater age distribution in wells producing mixed-age water (figure 2). Samples that fall below the curve indicate wells where a component of 'pre-modern' groundwater is present. Lines of equal percentage pre-modern can be calculated and used to estimate the degree of dilution of a contaminant that is captured in the post-modern component. Terrigenous He is examined and estimated for a geographic area in samples that are free of tritium. About 31% of the samples have radiogenic ^4He concentrations $>5 \times 10^{-8}$ ccSTP/g.

Excess Air Analysis

Noble gas concentrations were calculated based on the three physically-based conceptual models that have been used to interpret dissolved noble gas concentration data in groundwater (i.e., the unfractionated air model [1], the partial re-equilibration model [2], and the closed system equilibrium model [3]). For most samples, all models are able to adequately fit measured data within measurement uncertainty. Therefore goodness of fit is not a robust indicator for model appropriateness. The choice of interpretive model is important because parameters deduced from model output (recharge temperatures or ^3H - ^3He ages) systematically differ between models.

Samples from certain locations contained significantly higher Ne and excess air concentrations than are reported in the literature, with the maximum amount of excess air tending toward $0.05 \text{ cm}^3 \text{ STP g}^{-1}$ ($\Delta\text{Ne} \sim 400\%$). Samples not fit by the models tended to have greater than average Ne concentrations. The reason that models do not fit samples with large Ne concentrations may be non-equilibrium effects. Kinetic factors may control dissolved gas concentrations, especially in locations with high recharge flux. Excess air is less fractionated in samples with high excess air concentrations.

Trapping of gas present in the vadose zone via surface spreading during artificial recharge is the most likely source of the high excess air concentrations. The process by

DOI: 10.2312/GFZ.mga.040

which artificial recharge dissolves significantly greater amounts of atmospheric gases has important implications for oxidation-reduction dependent contaminant degradation. An improved understanding of the physical processes controlling gas dissolution during groundwater recharge is critical for optimal management of artificial recharge and for predicting the changes in water quality that take place during artificial recharge.

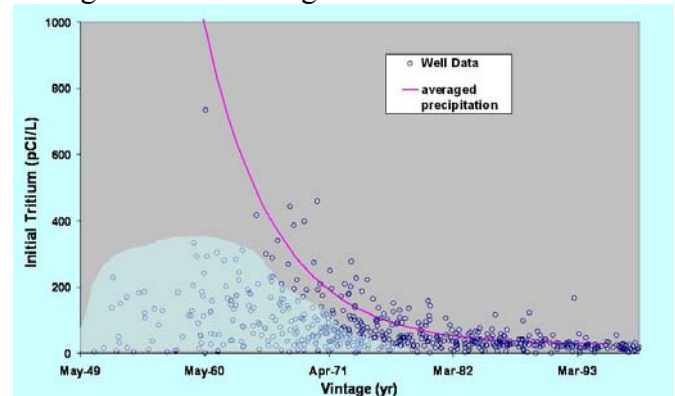


Figure 2. Curved line shows averaged tritium measured in precipitation at Santa Maria, California over the last several decades. Small open symbols represent wells from this study.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48. This work is sponsored by the California State Water Resources Control under the Groundwater Ambient Monitoring and Assessment program and carried out in collaboration with the U.S. Geological Survey.

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The Distribution of Tritium, Helium Isotopes, and Neon in Shallow Groundwater

Peter Schlosser^{1,2}, Martin Stute^{2,3}, Robert Newton², Brent Turrin², and Niel Plummer⁴

¹ *Departments of Earth and Environmental Engineering and Earth and Environmental Sciences, Columbia University, New York*

² *Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York*

³ *Department of Environmental Science, Barnard College, New York*

⁴ *U.S. Geological Survey, Reston, VA*

During the past ca. 15 years we measured tritium and helium isotopes on nearly 2000 groundwater samples covering a large range of hydrogeological settings. In this contribution, we analyze these data and discuss the main features of the overall distribution of tritium, helium isotopes and neon in shallow groundwater and discuss the implications of these features for the application of the tritium/³He method to dating of young groundwater. Most of the tritium concentrations fall into the range between 0 and 10 TU with some very high values indicating tritium contamination of samples that typically were collected near landfills. The mean $\delta^3\text{He}$ value is close to zero per cent, i.e., only slightly above the solubility

equilibrium with the atmosphere. The distribution of $\delta^3\text{He}$ ranges from close to -100 per cent indicating extremely high concentrations of crustal helium with its low ³He/⁴He ratios to several hundred per cent for samples with high tritium concentrations and high age or contributions of mantle helium. Most of the ⁴He concentrations measured in our samples cluster around $6 \cdot 10^{-8} \text{ cm}^3 \text{ STP g}^{-1}$, i.e., above the solubility equilibrium with the atmosphere. The Ne concentrations show smaller excesses above the solubility equilibrium with soil air. The frequent presence of significant ⁴He excesses reflects the fact that many of the samples we measured contain considerable amounts of crustal helium.

A New Noble Gas Paleoclimate Record from Texas: One Swallow Does Not a Summer, or Ice Age, Make

Chris M. Hall¹, Maria Clara Castro¹, Delphine Patriarche², Patrick Goblet³, Brian R. Ellis⁴

¹ U. of Michigan, Department of Geological Sciences, 2534 C. C. Little Building, Ann Arbor, MI 48109 - 1005

² Gaz De France, Département Géosciences, Service Appui Scientifique, 361 avenue du Président Wilson, 93211 Saint Denis La Plaine, France

³ Ecole des Mines de Paris, Centre d'Informatique Géologique, 77305 Fontainebleau, France

⁴ Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544

A generally accepted basic principle regarding the use of the noble gas thermometer in groundwater flow systems is that high-frequency noble gas climatic signals are lost due to the effect of dispersion. This loss of signal, combined with ¹⁴C dating issues, makes it only suited to identify major climatic events such as the Last Glacial Maximum (LGM) [1]. Consequently, the identification of significant noble gas temperature (NGT) cooling ($\geq 5^\circ\text{C}$) with respect to present time has systematically been associated with the occurrence of the LGM even when groundwater age controls were unavailable [1]. It has also become apparent at a number of studied sites that modern NGTs estimated through standard models are unable to reproduce ground temperatures at the interface with the unsaturated zone, a basic requirement for proper paleoclimate reconstruction through noble gases.

Bias to Low NGTs in Recharge Areas

A recent and detailed study in southern Michigan [2] found that estimated water table NGTs were systematically depressed with respect to ground temperature. These were estimated using the two most common and widely accepted models, i.e., the unfractionated air (UA) model [3] and the continuous equilibration (CE) model [4]. As demonstrated in [2], both models dis-

play differing ($2.5\text{-}4^\circ\text{C}$) but systematically depressed NGTs compared to ground temperature at the interface with the water table. A closer look at previously published NGT data indicates that at least in some cases, equally important biases are observed elsewhere. For example, temperature measurements in recharge waters of the Carrizo aquifer, southern Texas (see, e.g., [5]) indicate that previously reported NGTs [6] in this area are also depressed with respect to ground temperature by $\sim 4.2^\circ\text{C}$. This significant bias to low NGTs in recharge areas in very distinct climatic regions is a clear indication that assumptions of both the UA and CE models do not adequately describe all the mechanisms controlling noble gas concentrations and thus, NGTs in these areas. Instead, a systematic bias to low NGTs in recharge areas is observed. The Carrizo aquifer, in which the LGM was previously identified [6] and which presents an NGT bias of over 4°C , is an ideal setting to analyze and revise basic principles and assumptions.

Age Control and the Temporal Resolving Power of the NGT Record

We present a new noble gas data set (49 measurements) collected at 20 different locations in the Carrizo aquifer. This new data set together with previously published data (20 measurements) was used to cali-

brate a 3-D groundwater flow and ^4He transport model in which simulations of groundwater age were subsequently carried out. These account for mixing processes due to advection, dispersion, diffusion, and cross-formational flow. It is shown that samples that were previously attributed to the LGM belong in fact to the middle Holocene. A combined analysis of the impact of dispersion and the assumptions underlying competing NGT models indicates that groundwater flow systems, at least those with similar characteristics to that of the Carrizo, do have the ability to preserve short term (100-200 yrs) climatic fluctuations archived by noble gases.

Paleoclimatic Interpretation

The new paleoclimatic record shows that abrupt climate shifts during the mid-late Holocene which are associated with significant NGT ($\geq 5^\circ\text{C}$) changes do not reflect equally important changes in the mean annual atmospheric temperature (MAAT). Instead, these reflect the combined effect of atmospheric temperature changes, seasonality of recharge and, above all, significant variations of the water table depth which result from shifts between humid and arid regimes. Together with NGTs, our excess air record plays a critical role in identifying such abrupt climate changes. Specifically, the Carrizo combined data set indicates an abrupt shift from a cool, humid regime to a warmer, arid one at ~ 1 kyrs BP. A major Holocene (~ 6 kyrs BP) NGT cooling of 7.7°C with respect to present now identified is mostly the result of a dramatic water table drop following the ~ 1 kyrs BP transition period. Current NGTs in the Carrizo recharge area do not appear to be recording atmospheric changes. Rather, these are recording ground conditions reflecting mostly the impact of heat flow in the area. Observed systematic offsets in NGT recharge areas can be reconciled through NGT estimation models which account for a noble gas partial pressure increase in the unsaturated zone, possibly due to O_2 depletion.

Acknowledgments

Financial support by the U.S. National Science Foundation (NSF) Career Award EAR-0545071 and NSF grant EAR-0308707, is greatly appreciated.

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Groundwater dating with the aid of tracers: strategies, pitfalls and open problems

A. Zuber¹, K. Rozanski²

¹Polish Geological Institute, Carpathian Branch, ul. Skrzatow 1, PL-31560 Krakow, Poland

²AGH University of Science and Technology, Al. Mickiewicza 30, PL-30059 Krakow, Poland

Short-term multi-tracing versus time series of tritium

Transient tracers (^3H , $^3\text{H}/^3\text{He}$, ^{85}Kr , CFCs and SF_6) are commonly employed to investigate young waters in phreatic aquifers. Nowadays, two contrasting sampling strategies are in use: (i) several transient tracers are sampled over a short period of time, and (ii) tritium is sampled over extended period of time (up to several years) in addition to other tracers. The first approach is often favoured due to a short duration of projects. In such cases, the piston flow model (PFM) and/or binary mixing model (BM) is usually adopted to interpret the transient tracer data. The tracer age obtained from the PFM, called the apparent age, is regarded as hydrogeological parameter in spite of its inadequacy to yield residence time distributions (RTD) of converging flows in abstraction wells and springs. In contrast, tritium time series obtained in the second approach are adequately interpretable by box or numerical models, which yield RTD functions for individual sampling sites.

For wells abstracting young waters, very wide RTD functions are usually observed, which often lead to mixing between water containing transient tracer(s) with older tracer-free water. Mixing ratios of these two types of water can be obtained from the integration of the RTD functions [1, 2]. Such mixing ratios are time dependent and involve waters of the same chemistry. In practice, it is more important to identify mixing between waters of different origin, usually obtainable from stable isotope and Cl^- data, or of distinctly different ages. For instance, in one of the wells in the unconfined part of Cracow Malm limestones, tritium data yielded the mean age of 40 a

for the young component, and 70% of tritium-free water. The presence of that older component was confirmed only by relatively high $^4\text{He}_{\text{exc}}$ ($32 \times 10^{-8} \text{ cm}^3\text{STP/g}$) [3]. Similarly, in two of the wells in the unconfined part of Triassic carbonates in the Upper Silesia, tritium and $^4\text{He}_{\text{exc}}$ data also showed two-component mixing of modern water with much older pre-bomb era Holocene water. In both aquifers, $^4\text{He}_{\text{exc}}$ in other wells with modern waters was very low ($< 1 \times 10^{-8} \text{ cm}^3\text{STP/g}$), though components of the pre-bomb era were present as deduced from the RDT functions found from tritium data.

Disagreement of ages and models

For the $^3\text{H}/^3\text{He}$ method, the zero age is at the water table, whereas for the tritium method, the dating starts already at the ground surface. Consequently, both methods yield different ages. Similarly, the $^3\text{H}+^3\text{He}$ method is applicable only if the water table is very shallow. In other cases, the escape of tritiogenic ^3He from the unsaturated zone leads to false ages.

Combined interpretation of ^3H and ^{85}Kr is sometimes used to obtain both the age of water and the fraction of pre-modern water [4]. The same approach can be used for tritium combined with other gaseous tracer. However, one should keep in mind that this approach is valid only for shallow water tables. In other cases, ^3H yields ages which include the time of travel through the unsaturated zone, whereas for gaseous tracers that time is usually negligibly short. Consequently, interpretation based on the (gaseous tracer)- ^3H relationship for any specific model (usually PFM, EM or binary mixing model) will lead to false conclusions, as the RDT functions of both tracers

differ as being described by different models, such as EM for a gaseous tracer, and the dispersion model or the PFM in line with the EM for ^3H [1, 2].

Hydrodynamic age versus tracer age

Tracer and hydrodynamic ages often distinctly differ due to diffusion of tracers to stagnant water zones, such as the porous matrix in fissured rocks. However, they may also differ considerably in porous aquifers, if the flow patterns change. This stems from the fact that tracer steady state in the system is obtained after a much longer time than a new hydrodynamic steady-state resulting from a change in the withdrawal rate and/or a change in the recharge rate.

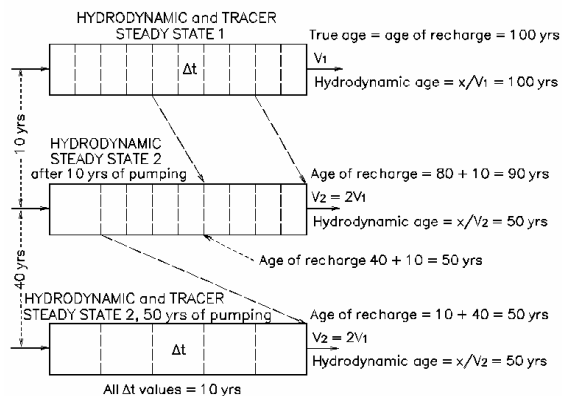


Fig. 1. Schematic model of three stages of piston flow through a column [2].

In the example shown in Fig.1 (upper row) both hydrodynamic and tracer ages are 100 years at the outlet. After 10 years of intensive abstraction a new hydrodynamic steady state is obtained (middle row), but any tracer will exhibit an unsteady age, greater than the flow age. Only after 50 years of withdrawal both ages are again the same, though much lower than those in the pre-exploitation era (lower row).

Much greater age differences may occur, if discharge by seepage changes to recharge as shown in Fig. 2, which roughly presents conditions of some wells described in [1]. Similar situation is also observed in Oligocene sands of the Mazovian basin, central Poland, which are recharged and drained by seepage through Pliocene silts and clays. In the central part, a multi-tracer

approach (mainly $\delta^{18}\text{O}$, $\delta^2\text{H}$, ^{14}C and ^4He) yielded ages above 10 ka, whereas the hydrodynamic modelling yielded ages below 1 ka [5]. These large age differences can be reconciled if one takes into account that intensive abstraction changed slow drainage rates to faster recharge rates. If the travel time of seepage is of the order of 0.8 ka, tracer ages observed in the Oligocene will remain the same or become even greater for a very long period of time [2].

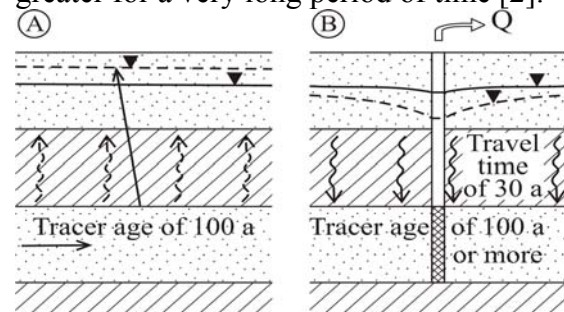


Fig. 2. When the abstraction starts, the hydrodynamic age may significantly decrease whereas the mean tracer age will increase due to back-flow from the aquitard [2].

Acknowledgements

Partial financial support to K.R. through statutory funds of the AGH University of Science and Technology (project No. 11.11.220.01) is kindly acknowledged.

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Conceptual models for dissolved noble gases in groundwater

W. Aeschbach-Hertig

Institute of Environmental Physics, University of Heidelberg, Germany (aeschbach@iup.uni-heidelberg.de)

Motivation

The partitioning of gases between groundwater and soil air is important for a variety of issues, such as the availability of oxygen, the fate of volatile contaminants, and the distribution of gaseous tracers. Several widely used environmental tracers are gaseous, e.g. CFCs, SF₆, He isotopes, ⁸⁵Kr, or ²²²Rn. The atmospheric noble gases are powerful tools to trace and study the gas partitioning and the related environmental conditions during groundwater recharge, because of their ideal conservative behavior and wide range of solubilities. Many noble gas studies have clearly shown the widespread presence of a gas excess above atmospheric solubility equilibrium (so-called "excess air") in groundwater. An increasing number of studies, however, report undersaturations, which are attributed to degassing [1,2].

Conceptual Models

A variety of conceptual models to explain the abundance patterns of dissolved atmospheric noble gases in groundwater have been proposed. Several of these models will be reviewed and presented in a new, coherent formulation. Both excesses and deficits of dissolved gases in groundwater can be explained by interactions with trapped gas bubbles. The concept of closed-system equilibration between groundwater and trapped bubbles (CE-model) proved successful in modeling excess air [3]. It can also be used to model the loss of dissolved gases that occurs if gas bubbles form in the subsurface.

The CE-model is not only more successful but also appears to be physically better founded than alternative models assuming a diffusion-controlled degassing process [1,4]. These latter models can often be ruled out based on the absence of diffusive isotope fractionation. Other models that have been proposed, invoking negative water pressures [5] or oxygen depletion in the unsaturated zone [6] as causes of excess air formation, still lack experimental evidence and need further investigation.

Experimental Tests and Applications

Although excess air and degassing have been frequently observed in field studies, only few dedicated studies of these effects have been conducted. Our research group is currently performing such experiments under controlled conditions both in the laboratory and in the field. Consistent and reproducible depletion patterns from several field sites using different sampling techniques confirm that degassing is not primarily a sampling problem.

A quantitative understanding of the patterns of dissolved noble gases in groundwater reveals information on the conditions and processes in the subsurface that influence gas partitioning. Excess air appears to be closely linked to water table fluctuations and related pressure variations in the recharge zone. Degassing could be due to the accumulation of geogenic or biogenic gases and/or a pressure decrease in the groundwater discharge area.

Interpretation of dissolved noble gas concentrations in groundwater using suitable

conceptual models and inverse modeling [7,8] enables a reliable description of the atmospheric gas components, i.e. the equilibrium concentrations modified by excess air or degassing. This provides an ideal basis for the determination of recharge temperatures. It is planned to re-examine data from older noble gas studies in the light of the new methods in order to establish a set of reliable noble gas paleotemperature records.

The quantitative description of excess air or degassing is also crucial for the calculation of gas tracer ages by the ^3H - ^3He , ^4He , and SF_6 methods. The inversion of complete noble gas data sets provides the ideal basis for the respective corrections. Even if such complete data are not available, the gas components relevant for groundwater age dating can be estimated within certain uncertainty ranges.

Conclusions

The CE-model is a versatile conceptual model for dissolved gases in groundwater, which appears to provide reasonable descriptions of both excess air and degassing phenomena. It presumably constitutes a sufficient and likely the best available model for the interpretation of most noble gas data sets in terms of recharge temperatures and tracer ages. The interpretation and use of excess air and degassing as indicators of environmental conditions during recharge and subsurface transport still require more research.

Acknowledgments

Data from several studies will be used, to which among others the following persons contributed: Petra Blaser, Hany El-Gamal, Laszlo Palcsu, and Martin Wieser.

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Session 3:

Noble gases in natural gas reservoirs

Understanding oil-gas-water systems, noble gas applications in reservoir characterizations/CO₂ sequestration, volcanic and seismically released gases, etc.

The use of noble gases for tracing fluid circulations in sedimentary basins: A case study of the Paris Basin, France

B. Marty, P. Burnard, R. Pik, B. Tibari, L. Zimmermann¹
M.C. Castro², S. Dewonck³, D.L. Pinti⁴, R. Kipfler⁵

¹ Centre de Recherches Pétrographiques et Géo-chimiques, UPR 2300 CNRS, 54501 Vandoeuvre lès Nancy France, bmarty@crpg.cnrs-nancy.fr

² Dept of Geological Sciences, Univ. Michigan, Ann Arbor, MI 48109-1005, USA

³ Agence Nationale pour la Gestion des Déchets Radioactifs, 1-7 Rue Jean Monnet, 92298 Châtenay-Malabry Cedex France

⁴ UNiv. Québec à Montréal, Case Postale 8888, MOnttréal, H3C 3P8, Canada

⁵ ETH Zurich, Switzerland

Introduction

Understanding underground fluid circulations in basins is essential for a variety of economic activities and their environmental impact. Because noble gases are chemically inert, their abundance and isotopic composition can only be changed by phase changes (e.g., solution of atmospheric gases in groundwater, gas-water-rock interactions), nuclear reactions producing noble gas isotopes and giving access to the geochronological dimension, and mixing between specific end-members (mantle, crust, atmosphere). Our group has been involved since 1990 in the study of noble gases in the Paris Basin, France. We present here a summary of these studies, aimed to better understand the origin, path, and residence time of fluids in well-characterized aquifers. The Paris Basin is an intracratonic basin that contains several permeable terranes allowing fluid circulation and/or storage (Fig. 1). From top to bottom in the basin, the aquifers are the Albian sandstone, the Dogger (Jurassic) limestone, and the Trias sandstone, which overlies the basement that formed during the Hercynian orogeny. The E-SE borders of the basin have been uplifted in the Tertiary during the Alpine orogeny, so that the general circulation path is from E-SE to N-NW, with recharge area being located in the Morvan and in Lorraine (where Nancy stands).

DOI: 10.2312/GFZ.mga.039

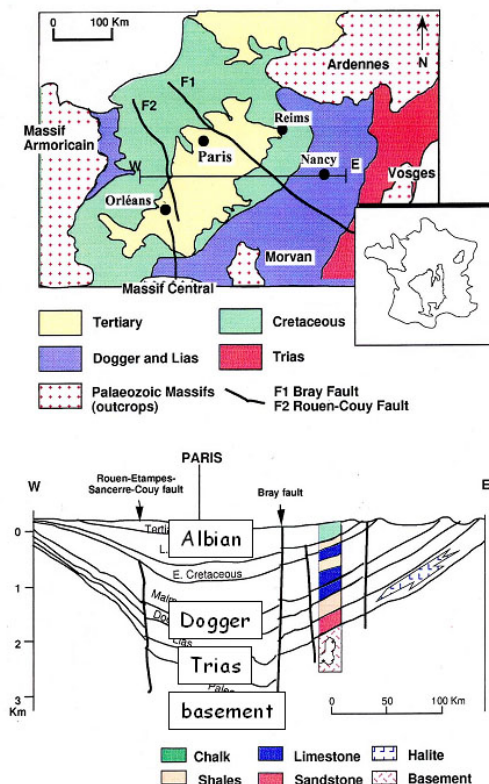


Fig. 1 : Summary of the Paris Basin geometry (adapted from ref. [1])

Fluid circulation in a multi-stored aquifer system

The most shallower aquifer of this study, the Albian sandstone, could be dated by ¹⁴C along a SE-NW flow line which allowed us to propose a temperature increase of 8-10 °C in central France since the last glacial maximum using noble gas paleo-

temperatures determined in ETH Zurich. He amount and isotopes along the flow line, together with water chemistry, indicate first internal radioactive production of ^4He in the aquifer, and then mixing with groundwaters from the underlying Neocomian aquifer towards the central area of the basin. Because ^4He correlates with water chemistry, we argue that the transfer of noble gases between the two superposed aquifers occurs by advection through the sandwiched aquitard, rather than by diffusion.

The fact that the He content of the different aquifers increases with depth can be regarded as a decrease of water movement with depth, assuming that the basin is now close to equilibrium in term of mass transfer. A model age of a few Ma for water in the Dogger aquifer is derived [2], which is in agreement with a pre-Quaternary stable isotope signature of the Dogger waters [3]. Correlations between salinity and geographical distribution of waters, together with ratios between noble gas isotopes produced by nuclear reactions (e.g., $^4\text{He}/^{40}\text{Ar}^*$ vs. $^{21}\text{Ne}^*/^{40}\text{Ar}^*$) in Dogger and Trias waters [1] are consistent with water mixing, rather than diffusive transfer, for mass transfer between the two deep aquifers. The distribution of these geochemical tracers together with that of salinity in the Dogger aquifer indicate that water mixing tends to occur in areas where major faults originating in the basement crosscut the sedimentary units.

Evidence for long term isolation between the Dogger and Trias aquifers in the East of the basin.

We have undertaken a study of the Trias aquifer from the eastern recharge area in the Vosges county towards the center of the basin through Lorraine. The evolution of ^{14}C ages versus distance from the recharge together with ^3He and ^4He concentrations indicates that the Trias aquifer is collecting mantle ^3He , in probable association with rifting in Alsace that marks the limit of the basin to the East and allowed

subvertical fracture and water circulation deep in the basement. The ^4He flux required to account for the increase of $[\text{}^4\text{He}]$ along the flow path is ~20 times that estimated for the quiescent basin center, and a factor of 2 that of the whole crustal production at the fractured border, consistent with episodic purging of the crust. The analysis of Dogger groundwater in the East above the Lias aquitard and the Trias aquifer shows that the mantle ^3He signal observed in the underlying Trias water has not yet reached the Dogger, which, together with other geochemical tracers, allow us to settle a confinement duration of 7 Ma for the Lias aquitard [4].

Conclusion

We propose that, in the case of the Paris basin, fluid mixing between the basement and the overlying aquifers occurs by advection through area affected by major tectonic accidents. The ^4He flux varies by one order of magnitude over the basin and is clearly tectonic-dependent. In one case, we have shown that an aquitard can isolate efficiently fluids for time lags of several Ma, provided that no major fracture system is present.

Acknowledgments

These studies were funded by the European Commission, the Agence Nationale pour le Gestion des Déchets radioactifs, the Institut National des Sciences de l'Univers (CNRS), and the Région Lorraine.

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Noble gases in brines from the St-Lawrence Lowlands, Quebec: tracing the origin of brines and associated hydrocarbons

C. Béland Otis¹, D. L. Pinti¹, A. Tremblay¹, M. C. Castro², C. M. Hall²,
V. Lavoie³, J. S. Marcil³

¹ *Département des Sciences de la Terre et de l'Atmosphère and GEOTOP-UQAM-McGill, Université du Québec à Montréal, Succ. Centre-Ville, CP 8888, Montréal, Québec, Canada, H3C 3P8*

² *Department of Geological Sciences, University of Michigan, 2534 C. C. Little Building, Ann Arbor, MI, USA 48109-1005*

³ *Junex Inc. 3075, chemin des Quatre-Bourgeois, Bureau 103, Québec, Québec, Canada, G1W 4Y5*

Introduction

Major sedimentary basins and Precambrian shields worldwide contain brines with salinities 10 times those of seawater [1, 2]. Some of these brines are Na-Cl type, while others are Ca²⁺-dominated. Although these brines have been studied for decades, their sources are not yet fully understood. Calcium excesses may in part result from albitization of plagioclase feldspars, which consumes dissolved Na⁺ and releases Ca²⁺, or dolomitization of calcite. The origin, ages, and migration of these brines are important to determine because they are often related to major oil and gas accumulations, as is the case for the North American craton.

Passive margin sequences of Potsdam-Beekmantown and Black River-Trenton groups of the St. Lawrence Lowlands in Quebec contain such Ca-Na-Cl type brines with very high salinities, ranging from 110 to 340 g/L. These stratigraphic units, deposited during the Cambrian-Ordovician along the eastern side of the continent Laurentia, are gas-prone, from the margin of Labrador to Texas. The origin and ages of the brines and their relation to natural gas and oil reservoirs is still unclear.

In Southern Quebec, brines and associated natural gas are found in domal structures of tilted blocks near normal faults oriented parallel to the St. Lawrence Rift system. The chemistry of major dissolved ions,

stable isotopes (δH , $\delta^{18}\text{O}$) as well as $^{87}\text{Sr}/^{86}\text{Sr}$ suggest an origin of these brines from ancient evaporated seawater likely modified by water-rock interactions with the crystalline Precambrian basement underlying the St. Lawrence Lowlands. Upward migration would have eventually relocated these brines up to the upper carbonate sequences of the Trenton Group. The age of these fluids is totally unknown. U-⁴He dating of similar brines circulating in the Precambrian Canadian Shield gave unconfirmed ages of 340 Ma [3].

Noble gas geochemistry

Noble gases can bring additional and precious information to the origin and migration of these brines and their relation to hydrocarbons. In this regard, a geochemical survey of these brines was initiated in the Bécancour region, Southern Québec. Sampled wells, with depths ranging from 960 to 1390 m, show salinities between 200 and 340 g/L. The Na and Cl are likely derived from residual seawater following halite precipitation while the source of Ca is still unresolved.

Noble gases (He, Ne, Ar, Kr, Xe) were analyzed in order to:

- 1) Determine whether the brine migrated from the crystalline basement, represents remnants of formation waters derived from the sedimentary cover or instead, result from a mixing of both.

- 2) Estimate groundwater residence time using U-⁴He method.
- 3) Determine whether these brines encountered potential gas or oil accumulation in the region, by studying elemental fractionation of atmospheric noble gases.

Preliminary results show ³He/⁴He ratios ranging from 0.13 to 0.25 R_a indicating the presence (1.9 to 3.7%) of mantle helium. The ³He/⁴He ratios are positively correlated with both depth and salinity of fluids. Similar ³He/⁴He ratios (up to 0.19 R_a) were found in brines circulating in the Trenton-Black River reservoirs in New York State and Pennsylvania [4]. The origin of mantle helium in Eastern North-America is not clear, but previous work suggested an aging magmatic source either from the Monteregian Hills (~120 Ma) or from magmatism related to late stages of the Acadian orogeny (~340 Ma) [5]. One of the sampled wells, in the proximity of a fault, has a particularly high ⁴⁰Ar/³⁶Ar ratio (2424), supporting the contribution of magmatic/mantle volatiles to some of these brines.

Acknowledgements

This work is being carried out with the support of Natural Sciences and Engineering Research Council of Canada through an industrial postgraduate scholarship #342297 to C. Béland Otis and NSERC Discovery Grants #314496 to D.L. Pinti and #105669 to A. Tremblay. We wish to thank R. Lapointe, G. Bach and L. Massé for assistance during sampling as well as the German Science Foundation (DFG) for travel funding.

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Noble gases in CO₂ rich natural gas fields

C. J. Ballentine¹, S. Gilfillan¹, Z. Zhou¹

¹ *School of Earth, Atmospheric and Environmental Sciences, University of Manchester, UK*

In addition to understanding mantle-derived volatile systems, CO₂ rich gas fields provide a natural analogue for understanding the fate of anthropogenic CO₂ that is to be injected into geological formations. We present noble gas and stable isotope data from most of the major CO₂ producing gas fields in the USA. We show that the CO₂ in these fields are all dominantly magmatic in origin, providing information about time of filling, and therefore reservoir age. We show that in almost all systems CO₂/³He is inversely correlated with groundwater-derived ²⁰Ne suggesting an important role for groundwater as a CO₂ sink. As the CO₂ is both chemically active and highly soluble in water, CO₂ may be removed from the gas phase by water-mediated precipitation, phase solubility or a combination of both these processes.

We present phase fractionation models that account for fractionation of the groundwater-derived noble gases and discuss these models in the context of CO₂/³He variation and stable isotope results. In particular we focus on extreme ²⁰Ne/³⁶Ar fractionation in some samples that cannot be explained by simple groundwater degassing. We focus on two models:

- i) prior modification of the noble gases dissolved in groundwater by interaction with an oil/hydrocarbon phase; and
- ii) two stage degassing and subsequent partial re-dissolution back into the groundwater system.

Mantle-Helium Distribution in Western Anatolia, Turkey: Relationship to Heat Distribution, Active Extension and Volcanism

N. Güleç¹, D. R. Hilton²

¹*Department of Geol. Eng., Middle East Technical University, 06531, Ankara, Turkey*

²*Fluids and Volatiles Laboratory, Geosciences Research Division, Scripps Institution of Oceanography, UCSD, La Jolla, California 92093-0244, USA*

Western Anatolia comprises one of the world's best known extensional terrains and is characterized by the presence of several moderate- to high-enthalpy geothermal fields located along the boundary faults of the major grabens. Helium-isotope compositions of geothermal fluids reflect mixing between mantle ($^3\text{He}/^4\text{He} = 8R_A$ where $R_A = \text{air } ^3\text{He}/^4\text{He}$; [1]) and crustal ($^3\text{He}/^4\text{He} < 0.1R_A$; [2]) components, the former ranging up to 45 % of the total helium in a given sample. There is a general positive correlation between the distribution of heat and helium in western Anatolia, suggesting similar mechanisms for their transfer to the surface. The fact that the mantle-He contribution in the vicinity of the Quaternary Kula volcanics is amongst the highest reported for western Anatolia ($2.8R_A$) further suggests that this transfer probably occurs in association with mantle melting accompanying current extension in the region. The spatial association of most of the high-enthalpy fields with the young alkaline volcanics (except in the Büyük Menderes Graben; BMG) is in support of this argument. On the other hand, the observations that i) there is a lack of volcanic exposures along the BMG (except at its western and southeastern terminations) where the highest values are recorded for both heat and helium, and ii)

relatively high mantle-He contributions occur in areas of not only the young alkaline, but also the old calc-alkaline volcanics, imply that the transfer of heat and helium may also be accomplished via plutonic activity. In this respect, the large range observed in the helium-isotope compositions may be linked with differential (local) extension rates and associated melt generation in the respective areas. This suggestion can be substantiated with a better regional coverage of He-isotope data which, unlike heat flow data, are currently restricted to point localities. Nevertheless, the present study suggests that the eastern segment of the BMG is a target locality for further studies from various disciplines concerned with active tectonics.

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Helium, Carbon and Geodynamics in a Regional Context: Central and Southern Italy.

D. Tedesco¹, R.J. Poreda², F. Tassi³ and O. Vaselli³

¹ *Department of Environmental Sciences, University of Naples 2, Caserta, Italy*

² *Department of Earth and Environmental Sciences, University of Rochester, New York, USA*

³ *Department of Earth Sciences, University of Florence, Italy*

Fluids associated with the central and southern quaternary volcanism and regional faults have usually $^3\text{He}/^4\text{He}$ ratio (as R_a) higher than crust with generally consistent associated $\delta^{13}\text{C}$. Fluids from volcanic [1] and natural environments are homogeneously distributed along the 600 kilometres of collection from south to north, from Sicily to southern Tuscany and west to east, from the Tyrrhenian coast line through the inner Apennine respectively. The $^3\text{He}/^4\text{He}$ ratio (R_a) shows a striking geographical distribution with a decreasing trend, from 6.0 to 0.01, from south to north while no particular differences have been detected in the west-east transect. Correlation between isotopic ($\delta^{13}\text{C}$ and R_a) and gas chemistry ($\text{CO}_2/^3\text{He}$ and $\text{CH}_4/^3\text{He}$) suggests that fluid(s) enter volcanic and fault systems directly from the mantle. Few exceptions are due to local surficial geological features, but no anomalous values, out of this characteristic trend, have been found. The main important feature, is that no large differences have been found in R_a ($\delta^{13}\text{C}$) between volcanic and natural gas samples located in nearby-latitudes. This result suggests a similar genesis and a general close-relationship, although the different geodynamic context, between He (and C) with local mantle signatures more than contamination by superficial crust or rich-atmospheric fluids. This finding shows

the importance of the link between, regional and local/regional tectonics, expressed as rock deep permeability and helium and carbon distribution over such a wide area. The decreasing trend from S to N is the evidence of a continuous evolution of the local upper mantle likely due to the nature of the subducting slab: oceanic crust in the S (Mt. Etna and Aeolian islands) versus a more pronounced continental U-rich crust going towards central Italy. To confirm our free-gas data, from some selected sites, helium data have also been obtained from fluid inclusions.

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Helium, Carbon and Argon in a Local Context: The Lake Kivu Area, East African Rift

D. Tedesco¹, R.J. Poreda², F. Tassi³ and O. Vaselli³

¹ *Department of Environmental Sciences, University of Naples 2, Caserta, Italy*

² *Department of Earth and Environmental Sciences, University of Rochester, New York, USA*

³ *Department of Earth Sciences, University of Florence, Italy*

On January 17, 2002 the city of Goma was partly destroyed by two of the several lava flows erupted from a roughly N-S oriented fracture system formed along the southern flank of Mt. Nyiragongo, DRC (Democratic Republic of Congo) [1]. A humanitarian and scientific response was immediately organized by international, governmental and non-governmental agencies coordinated by the United Nations [2]. Among the different scientific projects undertaken to study the Nyiragongo volcanic system and mechanisms that triggered this and possible future eruptions, we focused on chemical and isotopic analysis of gas discharges inside the Nyiragongo volcano and its surrounding areas. Gas samples from the summit crater have a clear mantle affinity in $^3\text{He}/^4\text{He}$ ($R/R_{\text{air}} \sim 7 \pm 1$) and $\delta^{13}\text{C}-\text{CO}_2$ (from -3.5 to -4.0 ‰) values. Similar mantle-like helium (6.8 - 8.2 R/R_{air}) is found in lake-side CO_2 -rich gas emanations (*mazukus*) with slightly lighter carbon values (from -5.3 to -6.4 ‰) [3]. The magmatic influence decreases at the bottom of Lake Kivu (5.5 - 3.0 R/R_{air}), and strongly in the southern side of the rift and peripheral gas discharges within and outside the rift (from 1.7 to 0.09 R/R_{air}). Similarly, $\delta^{13}\text{C}-\text{CO}_2$ ratios of peripheral gas emissions are lighter (from -7.02 to -8.44 ‰) or much lighter (from -10.48 to -11.63 ‰) than those from the crater, reflecting possible

degradation of organic matter. Our results suggest that the upwelling of mantle fluids is localized in a relatively small zone of the rift between Lake Kivu and Nyiragongo volcano, while crustal and biogenic fluids dominate peripheral and distal areas. This variation seems to be linked to both local and more regional tectonics. Our data do not show evidence of high $^3\text{He}/^4\text{He}$ signatures commonly associated with mantle plumes from this region.

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Noble gases in the crater lakes Nyo and Monoun, Cameroon

K. Nagao¹, M. Kusakabe^{2,5}, Y. Yoshida³ and G. Tanyileke⁴

¹ Laboratory for Earthquake Chemistry, Graduate School of Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan (E-mail: nagao@eqchem.s.u-tokyo.ac.jp)

² Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken 682-0193, Japan

³ Yoshida Consulting Engineer Office, Morioka-shi 020-0121, Japan

⁴ IRGM, B.P. 4110, Yaoundé, Cameroon

⁵ Present address: Korea Polar Research Institute, KORDI, Songdo Techno Park, 7-50, Songdo-dong, Yeonsu-gu, Incheon 406-840, Korea.

Introduction

After the gas disasters at Lake Nyo in 1986 and Lake Monoun in 1984, Cameroon, geochemical studies have been carried out to clarify the mechanism of the gas burst by measuring depth profiles of CO₂ concentration, pH, temperature etc. [1]. The CO₂ is being accumulated at the bottom layers of the lakes from an underlying magmatic source, as revealed from the carbon isotopic ratios of the dissolved CO₂ gas ($\delta^{13}\text{C} = -3.5\text{‰}$) [1]. Helium isotopic ratios $^3\text{He}/^4\text{He} = 8 \times 10^{-6}$ and 4×10^{-6} for Lake Nyo and Lake Monoun, respectively [2], also support the magmatic origin. We collected gas and water samples from various depths at both lakes in October 1999, January 2001, December 2001 and January 2003 (2 years after the artificial degassing at Nyo). Isotopic compositions of He, Ne and Ar as well as concentrations of all noble gases were measured to figure out depth profiles of noble gases and to compare them with other geochemical data obtained for both lakes.

Experimental method

Two collection methods were employed for gases dissolved in lake water: 1) gas exsolved from water in a Niskin water sampler was collected in a plastic bag and then transferred into a glass bottle with high vacuum stop cocks (in 1999), and 2) gases exsolved from various depths were directly collected in glass bottles through plastic hoses that had various intake depths (in 2001 and 2003). For noble gas analysis,

known amount of the gas was introduced into a vacuum line connected to a modified-VG5400 (MS-III) noble gas mass spectrometer. After purification of noble gases, Ar, Kr and Xe were retained on a charcoal trap cooled at the temperature of liquid nitrogen, then Ne was trapped on a sintered stainless steel trap cooled at 15K and He was measured. After the He analysis, Ne released from the trap at 45K was measured. Finally, Ar, Kr and Xe were released from the charcoal trap at 200°C and measured for Ar isotopic ratios and abundances of ^{40}Ar , ^{84}Kr and ^{132}Xe .

Results and discussion

Depth profiles of $^3\text{He}/^4\text{He}$ ratio for Lakes Nyo and Monoun are presented in Fig. 1. The ratios higher than the atmospheric value of 1.4×10^{-6} confirm the magmatic gas input to the lake water as already reported in [1, 2]. Though the ratios are almost constant in the depth ranges of 80-210m and 30-100m for Nyo and Monoun, respectively, the highest ratios of 8.2×10^{-6} and

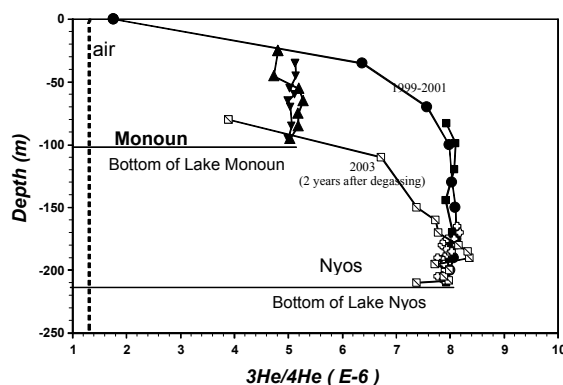


Fig. 1. $^3\text{He}/^4\text{He}$ depth profiles for the Lakes Nyo and Monoun.

5.2×10^{-6} were observed at 20-40m above the bottoms of Nyos and Monoun, respectively. No systematic differences among the profiles for 1999 and 2001 were observed, suggesting magmatic He input of constant $^3\text{He}/^4\text{He}$ ratios for both lakes. Decrease in $^3\text{He}/^4\text{He}$ ratios at the depths shallower than 150m observed for the samples collected in 2003 from Nyos was probably caused by the artificial degassing.

Fig. 2 compares $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for Nyos samples collected in 1999, January of 2001 and December of 2001. The ratios for samples of 1999 collected using plastic bags are systematically lower than those collected using pendent plastic hoses. The low ratios can be attributed to contamination from a small amount of air that remained in the plastic bag attached to the Niskin bottle, whereas $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in gases from the hoses were much higher with a maximum value of 600. Noble gas concentrations in CO_2 gas exsolved from waters are very low, e.g., $\leq 40\text{ppm}$ ^{40}Ar in CO_2 gas.

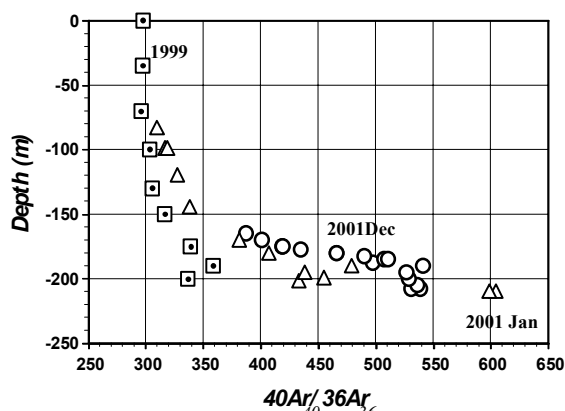


Fig. 2. Depth profiles of $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in Lake Nyos. The ratios for samples collected by different methods are compared.

The highest $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 600, observed in the bottom water in January 2001 just prior to the degassing operation at the Lake, seems to have disappeared in December 2001, 10 months after the degassing operation. Almost uniform $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (530-540) and $^4\text{He}/^{20}\text{Ne}$ ratios (~ 1100) between the depths of 195m and 208m in December 2001 are quite a contrast to those in January 2001. This may have resulted from the gas removal from bottom layer of the lake (203m). This in-

terpretation is confirmed in Fig. 3, where

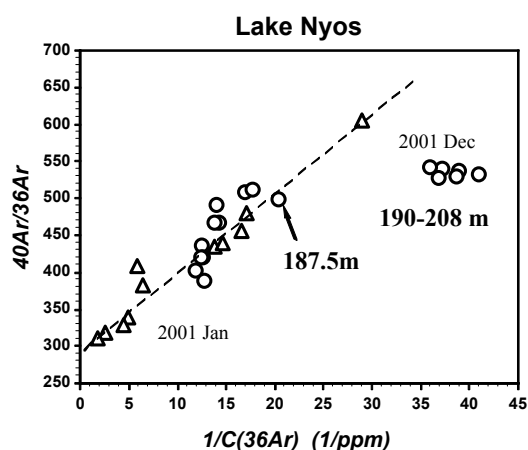


Fig. 3. Ar isotopic compositions for samples of January and December in 2001 are compared.

the Ar data points for January 2001 lie roughly on a single straight line, suggesting a simple mixing of atmospheric and magmatic Ar. While the data points for the depths 190-208m in December 2001 are plotted in a narrow area away from the line, showing low Ar concentration with almost constant $^{40}\text{Ar}/^{36}\text{Ar}$ of 530 in the bottom layer. The depletion of Ar in the bottom water might have been caused by the CO_2 degassing operation.

The gases from Lake Nyos with high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are accompanied by a small contribution of MORB-type Ne. These results indicate that magmatic gas is now being supplied to the bottom layer of these crater lakes with the incoming CO_2 gas.

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Variations in Helium and Carbon Isotopes and Relative Abundances in Geothermal Fluids of Western Anatolia, Turkey

Halim Mutlu¹, David R. Hilton², Nilgün Güleç³

¹*Department of Geological Engineering., Eskişehir Osmangazi University, 26480, Eskişehir, Turkey,*

²*Fluids and Volatiles Laboratory, Geosciences Research Division, Scripps Institution of Oceanography, UCSD, La Jolla, California 92093-0244, USA.*

³*Department of Geological Engineering, Middle East Technical University, 06531, Ankara, Turkey*

The aim of this study is to investigate helium and carbon isotopic compositions and associated CO₂/³He ratios of water and gas samples collected from 12 geothermal fields in western Anatolia. Based on the results of previous surveys in the region [1-2], the fields targeted in the present study are those where there is available enthalpy information but little or no He (and/or carbon) isotope data. The fields represent two regions: the northern part hosting the western extension of the North Anatolian Fault Zone (NAFZ), and the central part dominated by extensional grabens. The geothermal fields from the northern part are Tuzla, Kestanbol, Çan, Hisaralan, Manyas and Gönen, and those from the graben systems are Seferihisar, Balçova, Afyon, Gazlıgöl, Germencik and Kızıldere fields. Both natural springs and production wells were utilized during sampling. Gas samples were collected from high-enthalpy fields (Tuzla, Hisaralan, Seferihisar, Germencik, Kızıldere); with the exception of one sample taken from the steam phase in a production well, all the gas samples were collected as free gas phases from bubbling springs/pools. The R/R_A values (where R = sample ³He/⁴He and R_A = air ³He/⁴He) of the samples range from 0.27 to 1.67 and are significantly higher than the crustal production value of 0.02-0.05 R_A. Fluids with relatively higher R/R_A values are generally found in areas of significant heat potential. CO₂/³He ratios of the fluids exhibit a large variation (1.6x10⁹-2.3x10¹⁴) and are generally higher than that of the mantle (~2x10⁹). In comparison to waters, gas samples in the region are characterized by a

greater range of CO₂/³He ratios. The δ¹³C (CO₂) and δ¹³C (CH₄) values of fluids vary from -8.04 to +0.35‰ and -25.80 to -23.92‰ (vs. PDB), respectively. Oxygen-hydrogen isotopic compositions of the waters are consistent with the Mediterranean Meteoric Water Line and indicate a meteoric origin. Evaluation of He-C abundances together with the carbon isotope data indicates that degassing has significantly fractionated the elemental ratio (CO₂/³He); however, degassing may not be the major process affecting the carbon isotope variations. Mixing between the mantle and various crustal-derived volatile sources appears to be the main control on the C-isotopes. The temperatures calculated with various CH₄-CO₂ isotope geothermometers are around 334-371°C and are about 100-150°C higher than the estimates from chemical geothermometers. This suggests that either equilibrium is not attained for the isotope exchange reaction or the chemical composition of waters is easily modified by mixing with shallow waters: at this stage, the possibility of the achievement of isotopic equilibrium at levels even deeper than the geothermal reservoir cannot be ruled out.

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Noble gases in Jackson Dome gas deposits: identifying and quantifying natural CO₂ sequestration processes

Z. Zhou¹, C. J. Ballentine¹, M. Schoell² and S. Stevens³

¹ School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, UK

² GasConsult International L.L.C., USA

³ Advanced Resources International, USA

Jackson Dome natural CO₂ gas deposit, one of the deepest commercial CO₂ gas fields in the world, is located in central Mississippi, USA. It provides an important analogue for studying natural CO₂ sequestration process. We show in this presentation how noble gases can be used, together with other gases, to identify and quantify the origin, migration and sequestration processes of CO₂ gas in the Jackson Dome reservoir. We collected 10 gas samples from producing wells from Jackson Dome reservoirs. The Jackson Dome gas is dominated by CO₂, which ranges from 98.75% to 99.38%. The trace amounts of CH₄ and N₂ are correlated, and both correlate negatively to CO₂, suggesting that they have a common source. The greatest admix of N₂ and CH₄ is found on the crest of the trapping structure, however, the purest CO₂ is found at the field margins. ³He/⁴He ratios range between 4.27R_a and 5.01R_a (where R_a is the atmospheric value of 1.4×10⁶), indicating a strong mantle signature. CO₂/³He ratios vary between 1.07×10⁹ and 4.62×10⁹, they all fall in the range of the values found in pure magmatic samples (1-7×10⁹). ²⁰Ne concentrations correlate with resolved crustal radiogenic ⁴He concentrations, suggesting radiogenic noble gases also dissolved into groundwater before partitioning into the gas phase. The negative correlation between air-derived ²⁰Ne and CO₂/³He ratios shows that water plays a role in CO₂ sequestration, it can be responsible for more than 70% of CO₂ loss. The difference in mixing characteristics between the various gas reservoirs suggests that either the magmatic or crustal fluid end member varies from one system to

another over relatively short distances. ⁴⁰Ar/³⁶Ar ratios are between 4071 and 6420, the resolved radiogenic ⁴⁰Ar* contributes more than 90% of the total ⁴⁰Ar. The relationship among major gases (CO₂, N₂), ⁴⁰Ar, ⁴He and Ne isotopes shows that the gases in Jackson Dome reservoir are a mixture of a fractionated air component, a magmatic end member and a radiogenic/crustal component. Elemental fractionation of ²⁰Ne/³⁶Ar in the gas phase increased the ratio from 0.156 to between 0.798 and 1.35. CO₂/³He ratios correlate with both ²⁰Ne/³⁶Ar and δ¹³C (CO₂) values. We explored a variety of models to explain this data including: oil-groundwater partitioning; gas-groundwater partitioning; excess air dissolution and noble gas redissolution. A solubility controlled Rayleigh fractionation of groundwater modified by oil interaction can account for the correlations. In this case all the gases are dissolved in the groundwater on reaching the trapping structure. The concentrations of air-derived noble gases and other gas species (e.g. CO₂, CH₄ and N₂) also tell us the migration history of CO₂ gas in the reservoir. Relatively high concentrations of ²⁰Ne, ⁴He, CH₄, N₂ and low concentrations of CO₂ in gas samples from the centre of reservoir are consistent with the solubility partition of gases between gas and groundwater phases at the first degassing stage. At the later stages of the partition, gases with relatively high CO₂ concentrations and low ²⁰Ne, ⁴He, CH₄ and N₂ concentration fill the margin of the trapping structure. We are exploring other models to identify whether or not this concept provides a unique solution.

Session 4:

New or unusual applications of noble gases

*Tracing processes other than ground water transport/mixing, or paleoclimate:
new archives for noble gases (sediments, ice, speleothems), and applied tracers work
in environmental/ engineering systems, etc.*

Helium isotopes in sediments and ice – Tracers of eolian and cosmic dust

Gisela Winckler

*Lamont-Doherty Earth Observatory, Columbia University, 61 Route 9W, Palisades, NY 10964, USA,
winckler@ldeo.columbia.edu*

Helium in sedimentary archives is primarily derived from two sources: terrestrial continental dust rich in radiogenic helium and cosmic dust particles rich in implanted solar-wind helium (e.g., [1]).

The helium isotopic ratio of these two endmembers differs by about four orders of magnitude ($^3\text{He}/^4\text{He} \sim 2\text{-}4 \cdot 10^{-4}$ for the extraterrestrial vs. $\sim 1\text{-}3 \cdot 10^{-8}$ for the terrestrial endmember). By assuming the isotopic composition of the endmembers it is possible to calculate the relative contribution from each.

This makes the two isotopes of helium, particularly their combination, in many systems ideal proxies to monitor fluxes of continental and cosmic dust, respectively.

While ^3He -based studies of cosmic dust have been carried out covering a large range of time-scales from the Cretaceous to the late Quaternary, it is only recently that applications of ^4He as proxy of eolian dust have received wider attention. Potential archives for extracting ^4He -based dust flux records include marine sediments [2,3], ice cores [4], and corals.

Here I present case studies from different sampling archives with an emphasis on ^4He as a new tool for the study of eolian dust transport, environmental conditions of the dust source region and resulting implications for the interpretation of the paleoclimatic record.

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Quantitative analysis of noble gases in sediment pore waters : a new tool for paleoenvironmental studies

P. Jean-Baptiste¹, C. Chaduteau^{1,2}, E. Fourré¹

¹ LSCE, CEA-Saclay, 91191 - Gif/Yvette (France)

² DRO-GM, IFREMER, 29280 Plouzané (France)

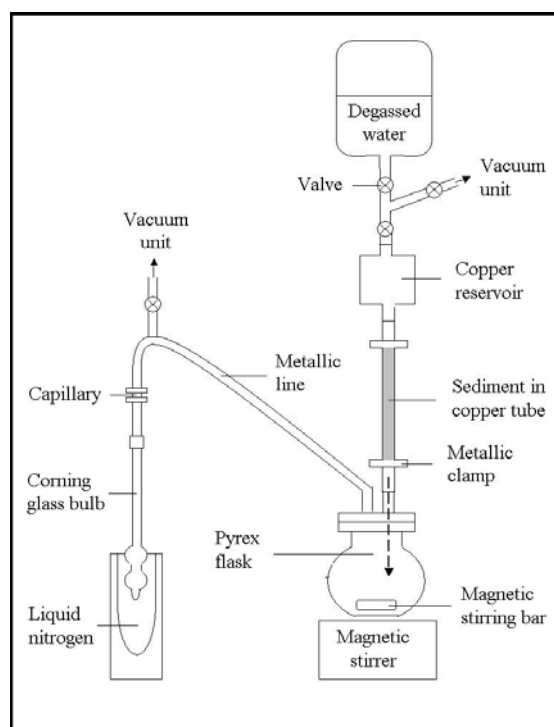
Noble gas dissolved in groundwaters have been used successfully for several decades for paleothermometry and groundwater dynamics studies [1-3]. In principle, sediment porewaters also have great potential as noble gas archives of paleoenvironmental changes, since noble gas concentrations in pore waters reflect the past conditions at the sediment-water interface at the time of water incorporation in the sediment.

However, in spite of this potential, their use has been hampered by the difficulties in collecting good samples due to gas loss and/or contamination problems [6-7]. It is only recently that these technical problems were overcome by transferring a sediment core section into copper tubes by squeezing [8]. In the lab, the sediment was heated and blown-out of the copper tube into an extraction line. With this technique noble gas from lake sediments, including Ne, Ar, Kr and Xe, have been used successfully as paleo-limnological proxies [9-12]. However, because sediment extrusion and extraction procedures implied elevated temperatures, some helium was released from the mineral phase of the sediment.

Here we present an alternate low temperature method which allows for accurate helium isotope determination. The principle of the method is to use copper tubes (1 cm OD/ 25 cm in length) to take mini-cores at both end of each core section. Sampling occurs immediately after each section cutting and before any other core manipulation. Then the copper tube is sealed with metallic clamps. Thus the core sampling is non-destructive (no squeezing) and can be

coupled with other samplings and physical measurements.

A specific line was developed to extract the dissolved gases from the sediment pore-water. The basic idea is to use pressurized gas-free water to push sediment out of the copper tube into a glass bulb. The degassed water reservoir is pressurized by flash-heating with a flame. Gas extraction from the liquid mud is then similar to what we usually do with water samples (see figure below).



Laboratory tests were first carried out with an artificial core made of sediment equilibrated with the atmosphere so as to have the porewater helium concentration at the solubility equilibrium. The sediment core was prepared as follows : marine sediments

were first washed and sieved (<0.2 mm). The sediment/water mixture was then allowed to rest for several days in a tank to remove much of the overlying water. The remaining water/sediment mixture was gently stirred with a mechanical stirring device for one week to equilibrate with ambient air at $20\pm 0.5^\circ\text{C}$. Then, the mixture (water content = 67%) was placed in a specially prepared 1.5 m long PVC tube (80 mm OD) kept vertical and closed at the bottom end with a plastic flange equipped with an o'ring. The PVC tube had multiple axial slits, 1 mm wide/50 mm long, made with a small circular saw. Each slit was covered with a small rectangular piece of filter paper fixed to the tube with adhesive tape. The entire tube was wrapped first with porous medical adhesive bandage, then with hygiene paper and finally with elasticated bandage. After three weeks of slow percolation of the water out of the tube (at $20\pm 0.5^\circ\text{C}$), the height of the sediment/water column was reduced by approximately a third, corresponding to a final water content of 55%. At this stage, the flange could be reopened and the core was sampled with copper tubes like a real sediment core.

The validity of the method was further tested at sea on three marine cores drilled during the Zairov cruise in the Zaire deep sea fan (Congo-Angola margin).

Both series of tests gave satisfactory results thus opening the field of helium isotopes geochemistry to continental and marine sediment pore waters. Detailed results and potential applications will be discussed at the conference.

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Evaluation of Argon-37 as a means for identifying clandestine subsurface nuclear tests

R. Purtschert¹, R. Riedmann¹, H.H. Loosli¹

¹ *Climate and Environmental Physics Division, Phys. Institute, Univ. Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland*

The verification of the CTBT (Comprehensive Nuclear-Test-Ban Treaty) relies on analytical tools for the identification and localisation of clandestine nuclear test explosions. Subsurface tests produce radioactive noble gas isotopes that may migrate in soil gases away from the detonation site and to the surface [1]. Measurement of these isotopes in quantities occurring above background levels are therefore strong indicators of a nuclear test.

For on-site inspections (OSIs) under the CTBTO, measurement of the noble gas Argon-37 was considered an important technique, as Ar-37 is a definitive and unambiguous indicator of a nuclear underground explosion. The probability to detect this isotope in air or soil gas samples collected during an OSI depends on many parameters. These include the calcium content of the medium surrounding the device, the characteristics of the neutron flux generated (it is noted that earthquakes do not produce neutrons, hence a natural triggering event produces no Argon-37), the existence of sufficient transport pathways for Argon to the surface and even the occurrence of low barometric pressure events which can enhance soil gas transport [1]. A reliable and definite identification of an UNE depends on a sound understanding of natural production and transport mechanisms of Argon-37 in the subsurface. From theoretical calculations it is known that the natural production rate strongly depends on

the depth below surface [2]. However, only few Argon-37 measurements are available from subsurface soil air. New data at different locations and lithologies are presented. Measured depth profiles of Argon-37 concentrations allow conclusions about the main production channels and transport mechanisms in shallow soils. This preliminary results indicate that natural Argon-37 levels in soil exceed background concentrations found in the atmosphere [3, 4] by several orders of magnitude. The depth stratification of Argon-37 in soils has important implication for the interpretation in terms of the identification of clandestine nuclear explosions. The potential of Argon-37 for remote sensing [3] will also be addressed.

Acknowledgments

This project is funded and supported by the CTBTO, Vienna.

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Fluid transport in low permeable formations at a geothermal site, Aachen, Germany

J. Lippmann-Pipke^{1,2}, U. Trautwein-Bruns³, S. Sindern⁴, T. Wiersberg¹,
S. Niedermann¹

¹ GeoForschungsZentrum (GFZ) Potsdam, Telegrafenberg, 14473 Potsdam, Germany

² Institute for Interdisciplinary Isotope Research IIF Leipzig, Permoserstr. 15, 04318 Leipzig, Germany

³ Geological Institute, RWTH-Aachen University, 52056 Aachen, Germany

⁴ Institute of Mineralogy and Economic Geology, RWTH-Aachen University, 52056 Aachen, Germany

Introduction

The analysis of the pore water composition of fresh drill cores with respect to stable isotopes (D, ¹⁸O), salinity and noble gas content has been shown to provide valuable information on fluid transport processes in geological formations. And especially in low permeable formations the application of isotope methods (including noble gases) is playing a key role - as shown in a variety of research projects [1-4, and others].

A current DFG-funded research program focuses on the comprehensive geoscientific investigation of the 2.5-km-deep geothermal well "RWTH-1" drilled in the city center of Aachen, Germany. The well sampled silt- and claystones with almost no porosity and permeability in the Carboniferous to Devonian lithologies [5]. Collaborators from GFZ Potsdam and the RWTH Aachen University jointly sampled fresh cores at the site and immediately sealed them in evacuated stainless steel containers according to the method described in [3]. The noble gas analysis of the pore water samples was performed at the noble gas laboratory of GFZ Potsdam as described in [6]. The K concentration measurement was performed at the Mineralogical Institute, RWTH Aachen.

Hydrogeological Setting

Aachen is located at the transition between the Variscan front and the Lower Rhine

Embayment. The area is seismically and hydrothermally active, which is related to the prolonged structural evolution characterized by compression and extension. Due to the various thermal springs already the Romans called the area "Aqua granni". Still, after 2000 years of utilization, the 45° to 75°C hot springs maintain their importance for Aachen as a well known Spa. Extensive literature exists on the hydrogeology, hydrogeochemistry and the genesis of these thermal springs [7, 8 and others].

Preliminary Results

Our sample suite consisted of seven pore water samples from freshly drilled cores and of five samples from cuttings covering a depth range of about 1000m between 1447m and 2544m below surface. The cutting samples proved to be unemployable for noble gas analysis, but six of the seven pore water samples from the cores revealed good results; one sampling container was leaky. The ⁴He concentrations of the six pore water samples from 1447m to 2544m depth amount to about 10⁻² cm³STP g⁻¹ with a negligible concentration gradient with depth. The ³He/⁴He ratios are around some·10⁻⁷. The sample with the least air contamination shows an ⁴⁰Ar/³⁶Ar ratio of about 500.

Although initially planned, no fluid samples could be obtained from the well due to lack of inflow from the formations.

Discussion

The preliminary ^4He concentrations in the pore water samples of this low porosity, virtually non permeable formation compare well with calculated concentrations resulting from production and diffusion after $(300\pm 100)\text{Myr}$. This very simple analytical calculation [9] is based on trace element concentrations of U and Th of 2.3ppm and 9.4ppm [10], a helium diffusion coefficient of $3.5\cdot 10^{-11}\text{m}^2\text{s}^{-1}$ [4], and a porosity of 0.01. We know that this concept is too simple, as the $^3\text{He}/^4\text{He}$ isotopic ratios of the pore water samples clearly show the influence of a mantle source: Therefore, in fact both crustal and mantle flux components need to be considered, with the consequence that the time needed to build up the measured helium concentrations in the pore water of the formations will become shorter than the above stated $(300\pm 100)\text{Myr}$. Based on the mantle end member value of $(7.42 \pm 0.03)\cdot 10^{-6}$ [11] the fraction of mantle derived He is estimated to amount to about 5%. A 2-D numerical model that considers in situ production, diffusion and flux components will be applied on the data and provide more realistic information on the model age of the pore water. First model results will be presented at the conference.

Acknowledgments

Enzio Schnabel is thanked for his extensive support in the noble gas laboratory at GFZ. Funding for this project was provided by the Deutsche Forschungsgemeinschaft (grants KU1476/2 and SI810/2) and the GFZ Potsdam.

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⁴He/Heat Flux Ratios as New Indicators of Past Thermal and Tectonic Events – New Constraints on the Tectonothermal History of the Michigan Basin

Maria Clara Castro¹, Delphine Patriarche², Patrick Goblet³, Lin Ma¹, Chris Michael Hall¹

¹ *University of Michigan, Department of Geological Sciences, 2534 C. C. Little Building, Ann Arbor, MI 48109-1063*

² *Gaz De France, Département Géosciences, Service Appui Scientifique, 361 avenue du Président Wilson, 93211 Saint Denis La Plaine*

³ *Ecole des Mines de Paris, Centre d'Informatique Géologique, 77305 Fontainebleau, France*

He/Heat Flux Ratio Indicator - Background

For over two decades it has been assumed that transport properties for both heat and helium are similar in the crust and that transport for both tracers is in steady-state [1]. Because helium and heat production results from a common source, these assumptions led to an estimated crustal He flux of $4.65 \cdot 10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$ based on heat flow considerations [1]. In addition, based on the observed low mantle He/heat flux ratio ($6.6 \cdot 10^{-14} \text{ mol J}^{-1}$) at the proximity of mid-ocean ridges, which is over an order of magnitude lower than the radiogenic production ratio ($1.5 \cdot 10^{-12} \text{ mol J}^{-1}$), it was concluded that the amount of U and Th required to support the oceanic radiogenic He flux would only provide ~5% of the mantle heat flux. Consequently, the presence of a terrestrial “helium-heat imbalance” was suggested [1]. Estimated ⁴He/heat flux ratios lower than radiogenic production ratios were thus interpreted as reflecting a He deficit in the crust or mantle original reservoir. To account for this “helium-heat imbalance”, the presence of a layered mantle (~670 km) was suggested in which removal of He is impeded from the lower mantle [1].

Recent Findings

By simultaneously carrying out 2-D simulations of groundwater flow, heat transfer and ⁴He transport in the Carrizo aquifer and surrounding formations in southwest Texas, the legitimacy of earlier assumptions was assessed [2]. Specifically, it was shown that the driving transport mechanisms for He and heat are of a fundamentally different nature for a high range of permeabilities ($k \leq 10^{-16} \text{ m}^2$) found in metamorphic and volcanic rocks at all depths in the crust. More specifically, it was concluded that total ⁴He/heat flux ratios lower than radiogenic production ratios do not reflect a He deficit in the crust or mantle original reservoir. Instead, they reflect the combined impact of air saturated water (ASW), advection, conduction, and diffusion when steady-state is reached for both tracers. The interplay between these different components and the extent to which each one influences this ratio depends in turn on hydraulic conductivities and therefore, permeabilities of the formations they cross in their movement upward, toward the surface.

Both, the presence of ASW (e.g., an atmospheric component provided by freshwater or seawater) in an advective dominated system ($k > 10^{-16} \text{ m}^2$), or ⁴He and heat transport in a diffusive/conductive dominated low permeability system will lead to

^4He /heat flux ratios lower than the radiogenic production ratio in a steady-state regime [2]. It was further concluded that only in the total absence of contact with ASW under a steady-state advective dominated regime for both ^4He and heat transport is the ^4He /heat flux ratio expected to equal the radiogenic production ratio. Simulations also suggest that ^4He transport is in a transient state in recently formed crust for permeabilities $\leq 10^{-17} \text{ m}^2$. Under these conditions ^4He /heat fluxes of up to several orders of magnitude lower than the radiogenic production ratios are expected.

In the absence of a thermal event, the maximum potentially observable ^4He /heat flux ratio is one corresponding to the radiogenic crustal production ratio. The occurrence of a ^4He /heat flux ratio greater than the crustal production ratio under all scenarios can only be the result of a past mantle or magmatic thermal event in which the released heat has already escaped while the released mantle He is still present in the system, and is slowly (with respect to heat) making its way toward the surface. These findings have given origin to a new indicator: the ^4He /heat flux ratio. This indicator is particularly useful to identify the occurrence of past thermal events in systems such as the Michigan Basin in which low hydraulic conductivity/ permeability but high thermal conductivity formations such as evaporites are present.

Helium-heat signature in the Marshall Aquifer, Michigan Basin

He concentrations and fluxes analyzed and estimated in the Marshall aquifer of the Michigan Basin revealed some surprising results [3]. Indeed, ^4He excesses are unusually high for such shallow depths ($\leq 300 \text{ m}$), and reach over three orders of magnitude above those of ASW. First order estimated ^4He fluxes in certain areas of the Marshall are far greater than those reported in other multi-layered basins around the world at far greater depths and also display $R/R_a \sim 0.15$ (R is the measured $^3\text{He}/^4\text{He}$, R_a is the $^3\text{He}/^4\text{He}$ atmospheric ratio) further

suggesting the presence of a more significant and local mantle component. Corresponding ^4He /heat flux ratios in these areas are also far greater than the crustal production ratio and point to the occurrence of a past thermal event of mantle or magmatic nature in which the released heat has already escaped and at least part of the released mantle ^4He remains in the system. We are currently expanding this noble gas study in the Michigan Basin to confirm this theory.

Acknowledgments

Financial support by the U.S. National Science Foundation (NSF) Career Award EAR-0545071, NSF grant EAR-03087 07, and the German Science Foundation (traveling expenses) are greatly appreciated.

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Behavior of gases during recharge below spreading ponds

Jordan F. Clark¹

¹*Dept. of Earth Science, University of California, Santa Barbara, CA 93106 USA; jfclark@geol.ucsb.edu*

A dual gas (SF₆ and ³He) tracer experiment and measurements of dissolved noble gases were performed at a managed aquifer recharge (MAR) site to examine gas transport and trapped air below an infiltration pond with a very high recharge rate (~4 m day⁻¹).

MAR is a recent advancement in groundwater/surface water management aimed at augmenting water supplies. This practice consists of recharging surplus surface water and reclaimed wastewater into aquifers at specially designed facilities for storage and later extraction. Often recharge occurs through infiltration or spreading ponds, which are small basins that are periodically drained and cleaned to maintain very high infiltration rates.

The study was conducted at the El Rio Spreading Grounds (Ventura County, CA, USA), which consists of ten shallow ponds (~3 m maximum depth) and a series of distribution channels. The local aquifer system is composed of discontinuous layers of gravel, sand, and silt and has generally been split into an upper and lower zone of production. Due to intensive pumping at nearby production wells, a regional groundwater depression is found surrounding the spreading grounds. Within this depression, local mounding beneath the ponds occurs during periods of recharge [1].

Artificial recharge at the El Rio Spreading Grounds has taken place since their construction in 1955 and, currently, about 40 x 10⁶ m³ of high quality surface water is recharged each year [1]. The seasonality in the recharge and production combined with the very steep local hydraulic gradients create a complex pattern of groundwater flow [1].

Noble gas samples were collected primarily for ³He analysis as part of the dual gas tracer experiment [2]. The experiment was begun on 27-Sept-02 near the end of a 35-day recharge event. Prior to this event, the ponds had been mostly dry for more than six months.

The concentrations of the heaviest noble gases in the pond were in equilibrium with the atmosphere and they were supersaturated in groundwater samples collected below the infiltration ponds due to the dissolution of trapped air. The excess air volumes ranged between 9 and 18 cm³/L (Fig. 1A) and averaged 13.7 cm³/L.

During the September recharge event, about 5 x 10⁶ m³ of surface water was recharged. Therefore, excess air formation dissolved about 7 x 10⁷ liters of trapped air. Assuming a porosity of 33% and a depth to water table of 12 m, air from more than 30% of the total pore volume dissolved. Hence, the amount of trapped air contained below the spreading ponds was significantly reduced during the recharge event. This reduction most likely leads to changes in the amount of excess air formed, with more forming early in the wetting cycle. Time series measurements at two nearby production wells support this assertion (Fig. 1A).

Noble gas recharge temperatures ranged between 20° and 13° C during the 7-month long study (Fig. 1B). The warmest samples were observed at the beginning of the study (Oct-02) and the coolest at the end (April-02). The temperatures were consistent with the season of recharge assuming a very short travel time.

Laboratory experiments have shown that gas transport in porous media is retarded by trapped air [3,4]. Although the

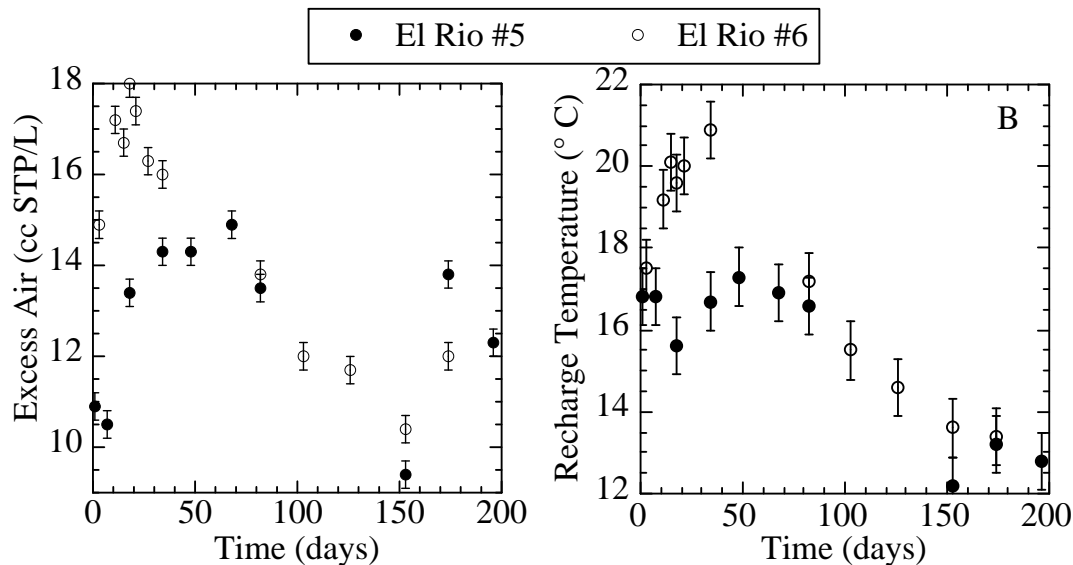


Figure 1: (A) Excess air and (B) noble gas temperatures from samples collected beneath the El Rio Spreading Grounds at two production wells, El Rio #5 and #6. Time zero is 27-Sept-06.

noble gas data clearly show that the infiltrating recharge water came in contact with trapped air, results of the dual gas tracer experiment suggest that loss and retardation of the gas tracers small was during the experiment [1]. First, the tracers were simultaneously observed at a nearby production well after only five days indicating that the leading edge was traveling at about 10 m/day. This is only slightly lower than the percolation rate. Second, the maximum SF₆ concentration was about 25% of the mean surface water concentration. Because of dispersion and because the well was probably drawing in both tagged and untagged groundwater, this very high concentration suggests most of the gas remained in solution during percolation. Third, breakthrough curves of SF₆ and ³He were similar indicating that the two gases were traveling at the same rate; SF₆ was not traveling 30% to 50% slower than ³He as expected if retardation by trapped air were significant. Fourth, more than 50% of the total SF₆ mass recharge was recovered at the eight nearby production wells. This very high recovery rate suggests that most of the SF₆ was transported to the groundwater.

The contradictory gas data – noble gases indicating the presence of trapped air and dual gas tracer data indicating little

or no trapped air – can be reconciled by postulating multiple flow conditions beneath spreading ponds. The tracer data indicates that gas lost during percolation is minimal and, therefore, a portion of the flow is through saturated columns. Excess air formation indicates the remainder of the flow passes (and partial dissolves) trapped air bubbles.

Acknowledgments

The noble gas samples were analyzed by G. B. Hudson. W. Aeschbach-Hertig assisted with excess air and noble gas temperature calculations. Supported was provided the UC Water Resources Center (W-962) and the University Collaborative Research Program at Lawrence Livermore National Laboratory (#03-GS-024).

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Noble gas geochemistry applied to CO₂ geological storage: Examples from French natural analogues

Battani. A.¹, Jeandel. E.¹, Deville. E.¹, Sarda. Ph.²

¹ IFP 1 4 avenue de Bois préau 92500 Rueil Malmaison, France

² Laboratoire de Géochimie des gaz rares, Université Paris Sud, Orsay, France

We made analyses of noble gases and associated major compounds (in this case almost 100% CO₂) with the $\delta^{13}\text{C}(\text{CO}_2)$ from different places from the French carbo-gaseous province. We also made some petrological and sedimentological observations of the travertines present in all different sampled places, to determine whether some significant part of the leaking CO₂ could be trapped at the Earth surface. The purpose of the study is to determine, using natural analogues, which context is most favourable for future CO₂ storage.

We collected seven gas samples from natural bubbling sources and geyser near Sainte Marguerite, Allier, France. This area is known to present an important heat flow anomaly, and the probable existence of a mantle plume just below. The site exhibits many CO₂-rich sources, with also giant "bubbles" forming always at the same place in the Allier river.

Back in the laboratory, we analysed the gas which is composed of almost 100% CO₂ with a $^{13}\text{C}(\text{CO}_2)$ of around -5‰ compatible with a mantle-derived origin. We analysed noble gas concentrations and isotopic ratios. The preliminary results show helium concentrations in the range of 0.28 to 8.22 ppm, with 5 samples lower than the atmospheric helium concentration of 5.24 ppm.

However, within these samples, the $^4\text{He}/^{20}\text{Ne}$ ratios -even low- (from 2.12 to 198)- all are greater than air value of 0.288;

thus air contamination can be discarded. The most intriguing result is that all our samples exhibit high and relatively homogeneous values of R/Ra, around 3.5 - 4, implying a large contribution of mantle-derived helium (R/Ra = 8 for the upper mantle, R/Ra around 6 for the SCLM) to the total budget of this gas.

The neon and argon isotopic ratios are not far from the atmospheric values, suggesting a small, if any, crustal contribution and an important Air Saturated Water (ASW) contribution, in agreement with this hydrothermalism. This is consistent with our very low total helium budget.

To our knowledge, this is the first time that so low helium concentrations combined with so high $^3\text{He}/^4\text{He}$ are measured in crustal fluids.

Our tentative interpretation is that gas comes from a degassing magma at depth, and then is transported to the surface as dissolved in water without accumulation. This is confirmed by the slight isotopic fractionation seen in the neon isotopes together with some elemental ratios, enriched in the lightest noble gas.

Acknowledgments

We thank Eric Tocqué and Yves Benoit from IFP to give us the opportunity to go on site and sample. Karine Le Pierres from BRGM is also thanked for the help provided on the field, as well as communications of previous results.

Migration of Noble Gas Tracer of Underground Nuclear Testing

Robert Annewandter¹, Martin Kalinowski¹

¹ Carl Friedrich von Weizsäcker Center for Science and Peace Research, Hamburg, Germany

Cyclical changes in barometric pressure can draw gas upward out of the soil into the atmosphere. In fractured permeable medium, the resulting transport process may be of orders of magnitude more significant than molecular diffusion [1]. Clandestine underground nuclear tests produces at depth of several hundred meters radionuclides, which migrate to the surface induced by this atmospheric pumping. A deep understanding of the transport mechanism is needful to state the estimated time of arrival for on-site inspectors of the CTBTO.

Acknowledgements

This work is funded by the German Foundation for Peace Research.

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He-isotope evidences in the basal layer of EPICA drill sites

R. Friedrich¹, D. Wagenbach¹, W. Aeschbach-Hertig¹, J. Schwander²,
S. Kipfstuhl³ and B. Stauffer²

¹*Institute of Environmental Physics, University Heidelberg, Germany*

²*Physical Institute, University Berne, Switzerland*

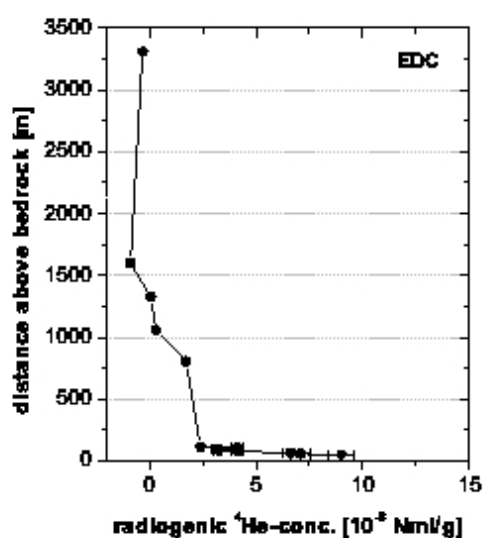
³*AWI-Bremerhaven, Germany*

Helium enters the ice sheet not only at the firn/ice transition, but also at the ice-bedrock interface. In contrast to other gases, He is highly soluble in ice and may undergo diffusiv transport within the ice sheet. Thus, we expect a significant basal layer enhancement of crustal He, which, similar to the temperature profile, is controlled by the competing transport processes of upward He diffusion versus downward ice advection. Knowing the profile of this mostly radiogenic He fraction would basically allow to place experimental constraints on the vertical ice velocity distribution in the near bedrock section. Vice versa, if the velocity profile is prescribed the (not well known) flux of crustal He may be inferred.

The high diffusivity of He causes variable, diffusiv He losses between core break off and final sealing of the ice sample that have to be accounted for. By taking multiple samples from the same depth and exposing them to selected degassing times, these problems could be overcome by using a 3D He-degassing model to estimate the initial He concentrations of the sample set as well as the respective diffusion constants D for ^4He and ^3He . Our studies show values of $D = (4.69 \pm 0.77)10^{-6} \text{ cm}^2/\text{s}$ for ^4He and $D = (5.19 \pm 1.14)10^{-6} \text{ cm}^2/\text{s}$ for ^3He . Similarly, solubility data were obtained from samples equilibrated at the drill site with ambient air.

Our first He ice sheet profile obtained at the Greenland summit (GRIP) revealed a

DOI: 10.2312/GFZ.mga.033



clear crustal $^3\text{He}/^4\text{He}$ signature showing up near bedrock, but surprisingly extending much higher up as could be explained by reliable scenarios of vertical ice velocity, crustal input and He diffusivity. Results from EPICA cores show no substantial difference in the mean ^4He levels compared to GRIP. Similar to GRIP, also both EPICA cores show remnants of the crustal (radiogenic) He signal far above bedrock, with EDML basal layer revealing the by far highest crustal He signal. The basal EDC He profiles stand out by unexplained, systematic variations, though respective simple age calculations are consistent with the current chronology.

Acknowledgments

We thank M.Huke for numerical model developments and S.Faria for careful field processing of the EDML bottom samples.

Noble gas measurements on fluid inclusions in stalagmites

Tobias M. Kluge¹, Werner Aeschbach Hertig¹

¹*Institute of Environmental Physics, University of Heidelberg, 69120 Heidelberg, Germany*

Background

Dissolved atmospheric noble gases in groundwater constitute a reliable paleothermometer, based on their precisely known temperature-dependent solubilities. The groundwater archive is limited due to the dispersive mixing and dating problems. In contrast to this, speleothems can be well dated using uranium-thorium dating. However there is no paleothermometer comparable to the noble gas thermometer so far. The idea of this project is to combine the advantages of both archives.

If noble gases are extracted from fluid inclusions in stalagmites, similar excess-air patterns than in groundwater can be detected. In case of groundwater the effect of excess-air can be corrected [1,2]. However, compared to groundwater, stalagmite samples have much less water (4 orders of magnitude), but a 100 times higher excess-air to water ratio. Therefore methods have been developed to account for this complication by trying to reduce the air/water ratio.

Methods and results

Noble gases have been extracted from stalagmites by crushing, respectively heating the sample in evacuated copper tubes. In the following step the amount of released water was determined using the water vapour pressure.

The extracted water amount is strongly dependent on the stalagmite (varying from 0.004 wt% (OBI 5, Austria) to 0.25 wt% (H12, Oman)) and on the extraction techniques (crushing, heating, microwave treatment). A typical value is 0.1% wt [3].

For the calculation of absolute noble gas amounts a diluted air standard is used. The statistical error for the standard is in the range of 1 - 2 %. Sample uncertainties have been much higher, because of a high and variable background and additionally in some cases low noble gas signals. Nevertheless the background corrected Xe-Ne and Ar-Kr plot are indicating that the values are not far away from the expected mixing between noble gases from water filled inclusions and some unfractionated "excess-air".

Outlook

Calculation of noble gas temperatures in case of the best samples (from a cave with a recent cave temperature of 26 °C) leads to 26, respectively 30 °C (although with very large uncertainties) using the same inverse modelling approach as for groundwater [1].

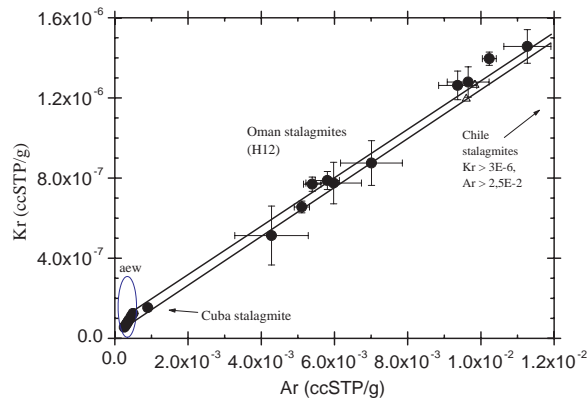
This may be a hint that noble gases from fluid inclusions can be used to determine noble gas temperatures if the problems (high uncertainties, high air/water volume ratios) can be managed.

The last experiments have shown that the selection of adequate samples is important. Without using special extraction techniques the air/water ratio is very different in case of various stalagmites. Therefore the samples should be checked in advance concerning the water content and the microscopic structure, which is related to the air/water ratio. For instance a stalagmite from Cuba has a surprising low air/water ratio. In those cases no special methods to reduce the excess air have to be applied with regard to the calculation of noble gas temperatures.

The calculation of noble gas temperatures

seems to be possible, if adequate samples with low air/water ratios are used and a sufficient measurement precision can be achieved.

Figures



Noble gas concentrations calculated for stalagmite samples. The points in the blue circle are values of air-equilibrated water at temperatures between 0°C and 30 °C. The black lines indicate addition of "excess-air" (upper line: water at 0°C, lower line: water at 30 °C). Most of the samples show ratios in the expected area, that means they are situated on the mixing line of equilibrated water with unfractionated air. However the uncertainties are quite large and typically in the range of 10%. Only the best sample has an uncertainty of 2-3 %.

Acknowledgments

This work is financially supported by the DFG (grant AE 93/3) as part of the DFG-Forschergruppe DAPHNE.

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Spatial variability in the release of terrigenous He from the sediments of Lake Van (Turkey)

Yama Tomonaga¹, Matthias S. Brennwald¹, Rolf Kipfer^{1,2}

¹Swiss Federal Institute of Aquatic Science and Technology (Eawag)

²Isotope Geology, Swiss Federal Institute of Technology (ETHZ)

The He in the atmosphere and the hydrosphere mainly originates from the solid Earth. The $^3\text{He}/^4\text{He}$ ratio can be used to distinguish He components originating from different compartments on our planet. In the atmosphere, this ratio is about 10^{-6} , in He produced in the crust it is about 10^{-8} , whereas in He originating from the mantle it is about 10^{-5} .

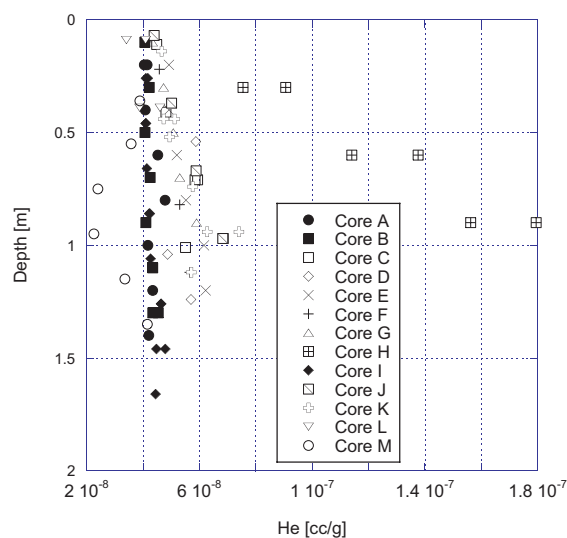


Figure 1: Concentration profiles in the sediment column.

He degassing from solid Earth occurs in a spatially heterogeneous manner and is focused on particular structures (e.g., fault zones, calderas, volcanoes). On local to regional scales, however, it is difficult to assess this spatial inhomogeneity of the terrigenous He flux by direct measurements. Recent analytical progress [1] allows for the first time He profiles in the pore water of lacustrine and oceanic sediments to

be analyzed, and we are able to interpret these profiles in terms of local He fluxes. This method provides a simple and direct approach to study the He emanation on small spatial scales.

The He profiles measured in 13 sediment cores (see Figure 1) from Lake Van (Turkey, see Figure 2) suggest that the He release from the sediments into the open water mainly occurs in the deep basin of the lake, which seems to be formed by an ancient caldera.

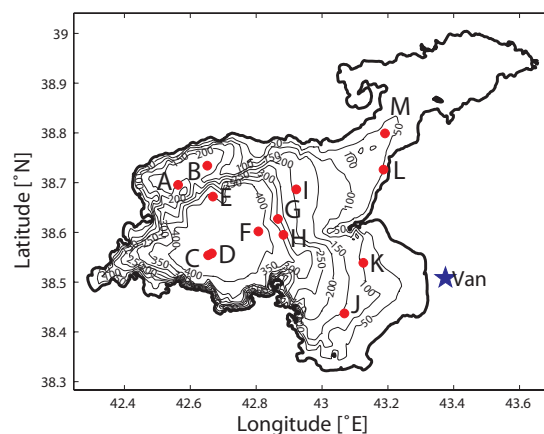


Figure 2: Lake Van bathymetry and sampling station positions.

The actual isotope signature of the terrigenous He accumulating in the open water body ($^3\text{He}/^4\text{He} \sim 10^{-5}$) indicates that this He is of mantle origin [3]. Furthermore, the He isotope ratios in the open water and in the sediment pore water suggest that there are at least two geochemical reservoirs which both inject isotopically light but different He into the lake (see Figure 3).

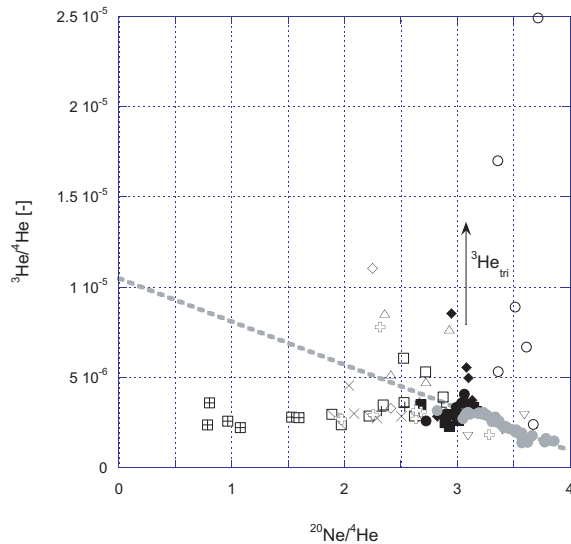


Figure 3: Three isotopes plot with ^3He , ^4He and ^{20}Ne . The grey circles represent the data from the water samples. The dashed line is the linear regression of the latter.

The fact that the He source found for the sediment samples has a lighter isotope signature than the source for the water body indicates that the sampled sediment cores are not situated near a quantitatively relevant emanation spot with respect to the entire He budget of Lake Van.

Acknowledgements

We want to thank Feray Gökdere, Dr. Mustafa Karabiyikoğlu and Prof. Dr. Sefer Örcen and the staff of the Yüzüncü Yıl University in Van for the great support during the expeditions in the last years. This work was funded by the Swiss Science Foundation (SNF 200020-109465).

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Hydrologic investigations of the Upper Ocean Crust: The 2008 Juan de Fuca Ridge Experiment

Jordan F. Clark¹, Andrew T. Fisher², James P. Cowen³, C. Geoffrey Wheat⁴, Keir Becker⁵, and Hans W. Jannasch⁶

¹Dept. of Earth Science, University of California, Santa Barbara, CA 93106 USA; jfclark@geol.ucsb.edu

²Dept. of Earth Science, University of California, Santa Cruz, CA 95064 USA; afisher@es.ucsc.edu

³Dept. of Oceanography, University of Hawaii, Honolulu, HI 96822 USA; jcowen@soest.hawaii.edu

⁴Global Undersea Research Unit, University of Alaska Fairbanks, AK 99775 USA; wheat@mbari.org

⁵Marine Geology and Geophysics, RSMAS, University of Miami, Miami, FL 33149; kbecker@rsmas.miami.edu

⁶MBARI, Moss Landing, CA 95039 USA; jaha@mbari.org

With the support of the National Science Foundation and the Integrated Ocean Drilling Program, an investigation of the hydrologic properties of the largest poorly characterized aquifer type in the world, the upper ocean crust, is planned for summer 2008. Earlier research indicates that the upper ocean crust is characterized by highly transmissive, fractured, chemically altered basalt [1]. Specific research objectives include quantifying (1) the magnitude and nature (distribution) of permeability and storativity, (2) fluid residence times, flow velocities and the associated solute and heat transport, and (3) the relations between fluid flow, microbiological community distributions, alteration, seismic properties, and the primary crustal lithology and structure.

The study will be conducted on the eastern flank of the Juan de Fuca Ridge and will utilize both existing (site 1027, 1027, and 1301) and new boreholes, creating a three-dimensional network of basement monitoring points, with borehole separation of 35 to 2500 m, for use in cross-hole experiments. The mean water depth of the site is about 2700 m bsl and approximately 300 m of sediment overlie the ocean crust. The boreholes will be cased through the overlying sediments, instrumented, and sealed using second generation CORKs. A variety of physical and geochemical approaches will be employed, including 24-hour slug and injection/flow tests and a multi-year deliberate tracer experiment.

A cocktail of tracer, which will include sulfur hexafluoride, rhodamine, microspheres,

and stained bacteria, will be injected into the seafloor during the 24-hour slug test. Following the injection, an equal or greater volume of tracer-free seawater will be introduced to the borehole, which will subsequently be sealed. The natural gradients should readjust quickly following the initial perturbation. Critical to the deliberate tracer experiment is subsequent recovery of tracers. OsmoSamplers, a passive pump system, will be installed in each bore hole and collected at the seafloor 1 to 5 years later using a submersible. OsmoSamplers are long-term, low volume (~1 ml/day) fluid collectors, which consist of an osmotic pump that continuously draws water into a long (~1-2 km), narrow diameter (~1 mm ID) piece of tubing [2]. In the laboratory, the tubing will be subdivided into the equivalent of week-long pieces, from which the water will be extracted and analyzed for tracer concentrations. Using the constructed tracer breakthrough curves, hydrologic transport properties will be estimated.

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Session 5:

Technical advances in noble gas analysis

New analytical methods and systems, data quality issues, etc.

Towards developing the capability for near-continuous sampling and storage of helium in geothermal fluids from regions of crustal unrest

D.R. Hilton¹, E. Furi¹, M.D. Tryon¹, A.L. Labonte¹, and K.M. Brown¹,

¹Geosciences Research Division, Scripps Institution of Oceanography, La Jolla, CA 92093-0244, USA.

Helium isotopes have great potential in studies related to seismic or magmatic activity. Their utility stems from the wide range in isotopic ratios between mantle-derived He ($^3\text{He}/^4\text{He} \sim 8R_A$ where $R_A = \text{air He}$) and He produced in crustal lithologies by radiogenic decay ($0.02R_A$). Consequently, changes in crustal properties (e.g., permeability) or instances of magma movement, related to either seismic or magmatic unrest, can upset the balance in He inputs from mantle and crustal endmembers resulting in easily-perceived variations in $^3\text{He}/^4\text{He}$ ratios in crustal fluids such as groundwaters and geothermal waters.

There have been some notable successes in correlating variations in $^3\text{He}/^4\text{He}$ with the timing, locations and magnitude of earthquakes and volcanic eruptions. For example, (Sano et al., 1986) observed increases in $^3\text{He}/^4\text{He}$ ratios associated with the 1984 western Nagano earthquake in Japan. In a different study, monitoring of Izu-oshima volcano revealed large increases in $^3\text{He}/^4\text{He}$ of geothermal fluids (from ~ 1 to $5R_A$) following magmatic activity in 1986 (Sano et al., 1995). Italiano and Martinelli, (2001) reported doubling of $^3\text{He}/^4\text{He}$ values (from 0.02 to $0.04R_A$) at Umbria-Marche in the central Apennines, Italy following a seismic crisis in 1997-98. In addition to these examples of He responding in a positive fashion to crustal activity, there are many other cases where He-isotopes show little or no variations in spite of persistent volcanic/magmatic unrest. For instance,

studies at Long Valley Caldera from 1986-88 (Hilton, 1996) and along the North Anatolian Fault Zone (NAFZ) from 2002-04 (De Leeuw et al., unpublished data) revealed virtually constant $^3\text{He}/^4\text{He}$ ratios throughout monitoring periods of ~ 3 -years duration.

There are numerous factors that could influence whether He-isotopes respond to crustal disturbances, e.g. magnitude of seismic/magmatic event, distance between event and sampling point, hydrologic controls on fluid mixing, etc: however, one variable which is just as important for recording changes in $^3\text{He}/^4\text{He}$ values is frequency of sampling. In the study of Italiano and Martinelli (2001), the adoption of a weekly sampling regime was able to catch the He-isotope perturbation following the seismic crises prior to $^3\text{He}/^4\text{He}$ ratios returning to normal background values within 2 months. Not all He-isotope anomalies are so short-lived, however: Sano et al. (1995) estimated a time-constant for return to pre-seismic He-isotope values of ~ 15 years following volcanic activity at Izu-oshima. It is unknown if the 3-monthly sampling frequency adopted at Long Valley and the NAFZ missed any short-lived He perturbations: sampling/analysis frequency in these cases was limited to 4-times per year.

If He-isotopes are to realize their full potential as a precursory tracer of crustal unrest then a new approach is required that is capable of producing a near-continuous record of He-isotope changes in a natural

system without recourse to high frequency (and expensive) sampling. In effect, what is required is an approach that utilizes continuous sampling together with preservation of fluids - to enable specific times of interest (e.g. immediately prior to and/or following a crustal event) to be targeted for detailed, follow-up analytical work. In this way, it should be possible to recognize any anomalous He-isotope signals over a monitoring period irrespective of their duration.

We have developed such a system for deployment on natural cold seeps in the submarine environment. The device consists of a modified CAT-meter (Chemical Aqueous Transport meter; see Figure 1 and description by Tryon et al. (2001). The modification involves the addition of a second osmotic pump, high pressure valves, and copper sample coils to collect and store a temporally-resolved continuous water record for later dissolved He (+ other gases) analysis. The copper coils have virtually zero permeability for He and are held at sea bottom pressure on recovery so that gas losses are negligible. The plastic sample coils are used to collect fluids for non-gas aqueous chemistry and to enable calculation of fluid flow rates. The major ion and flow rate record assist in identifying periods of interest for the more expensive and time consuming gas analyses.

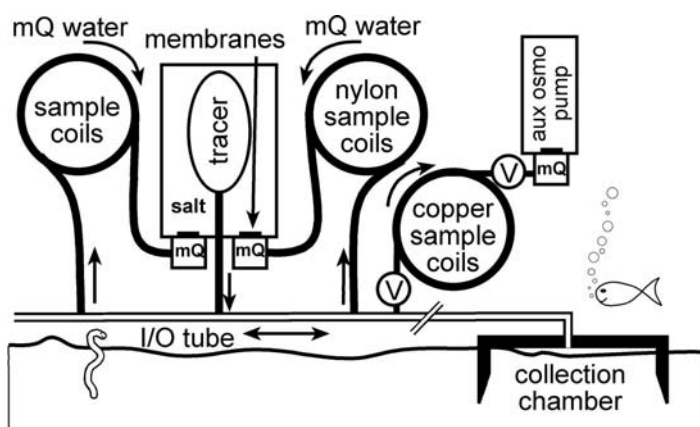


Fig. 1: Schematic of CAT meter. Enhancements to the original CAT meter include the addition of a secondary osmotic pump, copper sample coils, and

high pressure valves which automatically shut off on release from the sea bottom.

We have deployed the modified CAT-meters at the Extrovert Cliffs site in Monterey Bay, California (Martin et al., 1997). The area is situated close to several active strike-slip faults, including the Monterey and San Gregorio fault zones, and it has many cold seeps located at ~1000m depth. Deployments took place in 2004 and were of ~ 1-3 months duration. Copper coils were processed for both helium and CO₂ (isotopes and abundances) using conventional laboratory methods described previously (Shaw et al., 2003). All samples are supersaturated with respect to seawater in helium and carbon dioxide indicating addition of extraneous CO₂ and He. The main features of the results can be summarized as follows:

- 1) Air-corrected ³He/⁴He ratios vary between ~ 1R_A and 2.4 R_A, i.e. between values expected for mantle-derived He (8 R_A) and radiogenic He produced in crust and/or sediments (0.02R_A). Using a simple 2-component mixing model for He, up to ~25% of the total He is mantle-derived..
- 2) For most samples, the CO₂/³He ratios are significantly greater than anticipated mantle values (MORB ~ 2 × 10⁹).
- 3) There is large range in δ¹³C values from -5‰ to ~-25‰. This is consistent with an input of both organic-derived carbon (δ¹³C ≈ -30‰) and mantle-derived CO₂ (δ¹³C ≈ -6‰).

Perhaps the most significant result of our deployments, however, is the record of the temporal variation of the He and CO₂ concentration as well as the helium and carbon isotopic composition preserved in the coils. The data demonstrate remarkable temporal variation over days/weeks in the volatile content of the cold seep fluids (Fueri et al., 2005) – these results will be presented at the meeting.

Subsequent to our initial analytical effort, we have refined our laboratory procedures and constructed a dedicated extraction system which can be interfaced directly to the noble gas mass spectrometer. In this way, we can obtain He-CO₂ results on significantly smaller quantities of fluid (< 1 cm³) thus dramatically improving our time-resolution on He-isotope analysis. Using different sections of the same Monterey coils, we have now obtained a total of 10 combined He-CO₂ analyses which cover a total time period of 1 day (i.e. sampling was achieved with a frequency of ~2.5 hours). Corrected ³He/⁴He ratios vary between 1.4 and 3.4 R_A over a single day.

The Monterey results show an unprecedented level of sampling frequency for He-isotopes. The results offer the exciting prospect that geothermal fluids can be collected on an almost continuous basis, with storage for later He analysis at a frequency determined by the seismic or volcanic record. We are presently evaluating the Monterey results with the aim of understanding the processes regulating the inputs (earthquakes, tidal influences, etc.). The next challenge is to adapt the CAT-meters so that they can be used on groundwater wells and subaerial cold and hot springs.

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A New Noble Gas Facility for Isotope Hydrology at the International Atomic Energy Agency Vienna

Axel Suckow, Manfred Gröning, Manfred Jaklitsch,
Lian-Feng Han, Pradeep Aggarwal

International Atomic Energy Agency, Wagramer Strasse 5, A-1400 Vienna, Austria

In early 2003 the International Atomic Energy Agency (IAEA) began installation of a noble gas facility. Since noble gases have proven to be an important tool in modern isotope hydrology, installation of such a facility at IAEA aims primarily to strengthen the use of the T/³He dating method in groundwater studies. Besides that we want to further develop methods using helium as a tracer in groundwater beyond the time scale of the application of tritium, to use noble-gas derived recharge temperatures as constraining parameter both to derive the origin of groundwater and to better correct for excess air in T/³He dating and finally to improve the detection limit of tritium by the ³He ingrowth technique.

Any setup for the above goals directly defines targets for the system to be installed: it has to be capable of measuring the ³He/⁴He ratio and it should be able to handle any type of sampler routinely used in groundwater studies, may it be the typical pinch-off copper tubes or passive samplers. It has to be able to handle samples with higher load of reactive gases like CO₂, CH₄ etc. and to measure samples with helium contents several orders of magnitude above solubility equilibrium. It should be able to measure as many of the heavy noble gases argon, krypton and xenon as possible. The larger sample numbers per site in modern studies makes a high sample throughput desirable. This in turn needs high degree of automation with simultaneous parallel measurement of different gas components in different mass spectrometers and also

points towards an off-line extraction system.

We studied some of the established approaches of noble gas measurement and tried to combine as many well proven techniques as possible to reach the targets defined above. Nearly four years later the facility consists of a MM5400 sector field mass spectrometer plus two quadrupole mass spectrometers (QMS) and a very recently finished off-line extraction system for 10 samples in parallel in one run. An eight-fold multiport and a calibration system using aliquots of air is connected to a noble gas purification system that consists of traps and getters and one QMS, similar to the installations in Zürich and Salt Lake City. This purification system will be dedicated to measuring the heavy noble gases, but it can be bypassed to a cryo purification and cryo charcoal trap system similar to the oceanography-dedicated installations in Heidelberg, Bremen and Lamont. Behind these cryo traps a precise spinning rotor gauge (SRG) together with a system of split volumes allows us to determine the absolute helium concentration and to partition large helium amounts. This ensures that the signal range for ³He/⁴He determination in the MM5400 sector field mass spectrometer is less than a factor of five for ⁴He. Simultaneous to the helium measurement, the neon fraction is desorbed from the cryo trap, the absolute Neon concentration is measured with the SRG and the ²⁰Ne/²²Ne isotopic ratio determined in the second QMS.

The measurement system is controlled by our own software “NobleControl”. Written by one of us (A.S.), it is a very modular code in LabView that runs under MS Windows XP and can be easily adapted to new hardware. Very flexible control over the measurement process itself is possible in NobleControl with a script language having the typical syntax features of present day high-level programming languages including Variables, Repeat and While loops and nested blocks. It also allows the parallel processing of several command queues and the communication between these tasks by messages. A typical sequence in our actual approach comprises seven command queues. They control the measurements of the three mass spectrometers, the gas inlet, the cryo purification, manual commands and a master dispatch queue. All system state parameters like pressures, valve states, temperatures, MS signals etc. are stored at user-defined intervals and can be displayed during the run. The typical amount of data produced from a one-day run is around 20 MByte as ANSI text files. Post-processing is achieved using a noble gas dedicated sub-system of the LabData laboratory management and database system. With a MS SQL Server backend and a MS Access front end and graphical user interface LabData imports needed data, computes signals at inlet time and evaluates measurements during preparation like the absolute gas amounts from the SRG. To compute absolute gas concentrations, system efficiency, background and linearity is evaluated for each of the noble gas species in question (^3He , ^4He , ^{20}Ne , ^{22}Ne ...). Algorithms to convert measured concentrations into simple $T/{}^3\text{He}$ ages or into mean residence times using lumped parameter models were part of the LabData system already before 2003. Algorithms to deconvolute heavy noble gas concentrations to determine infiltration temperatures and excess air are in preparation. Both NobleControl and LabData are open source codes and the entire software is available free of charge for other groups.

To date we have achieved an internal reproducibility, defined as the standard deviation of the efficiency (signal/ccSTP) of air aliquots through the whole measurement process over six weeks, of better than 1.5% for ^3He and better than 1% for ^4He , ^{20}Ne , ^{22}Ne . A typical gas inlet (reference air split or unknown) is processed through the whole system within 45 minutes. This is comparably slow for helium and neon measurement only and can be further optimized. But it is to be expected that during future runs including the measurement of heavy noble gases one hour will be a typical time for the whole process. We aim for the full processing of noble gases of eight unknowns within an automated 24h-run. The script controlled inlet system has shown to operate samples with helium concentrations of five orders of magnitude above solubility equilibrium in routine automated mode. Such high amounts of helium are splitted automatically where each split reduces the helium amount by a factor of 2.62 and needs 5 minutes. Test measurements using passive samplers equilibrated under laboratory conditions show to agree well with the expected values of helium and neon concentration and to better than 1% and 0.5% respectively with the expected helium and neon isotope ratio. The first water samples to date (December 2006) are processed by the off-line extraction system. The next steps are the investigation and optimization of parameters of the extraction system (first half of 2007) followed by the necessary steps to measure concentrations of argon, krypton and xenon in automated mode. Probably we will further increase precision in future using isotope dilution spikes.

Acknowledgments

We very much appreciate the support and information received from existing noble gas laboratories namely Bremen, Heidelberg, Lamont, Salt Lake City and Zürich.

Development of a new facility for dating old ground waters and ice cores using ^{81}Kr .

B. Lavielle¹, E. Gilabert¹, B. Thomas¹ and V. Lavastre^{1,2}

¹University Bordeaux 1-2, Chimie Nucléaire Analytique et Bioenvironnementale (CNAB), UMR 5084 CNRS, Le Haut Vigneau, BP120, 33175 GRADIGNAN Cedex, FRANCE

²Geochimie Isotopique Environnementale – GIS/CEREGE, UMR 6635- Nîmes University, FRANCE

Krypton-81 is produced by nuclear reactions induced by cosmic rays in atmosphere while Krypton-85 is released from nuclear installations. With respective half-lives of 229 ky and 10.76 y, these isotopes are considered as ideal tracers for dating groundwater or ice core [1-6]. The measurement of ^{81}Kr from a groundwater sample was first demonstrated using several isotopic enrichment steps followed by RIS-TOF technique [1-3]. Due to the very low abundance of ^{81}Kr in groundwater – 1200 atoms/l in modern water – the dating generally requires sample volumes of at least several hundred liters [5,7]. Since 2003, in a collaborative work with IRIM, CNAB is developing a set of four instruments in order to measure ^{81}Kr in groundwater using reasonable volume of water (20 l). Each instrument is dedicated to perform important steps in the dating process:

- 1) A vacuum line is designed for gas extraction from water, Kr separation and purification. It includes a 50 l vaporization tank, 4 gas chromatography columns and getters.
- 2) A first mass spectrometer is dedicated to the ^{81}Kr and ^{85}Kr enrichment process is building. It consists in a modified HR-ICP-MS in order to perform high ionization efficiency and high mass resolution with large Kr samples. Selected ions are implanted in a thin Al layer on sapphire targets.

- 3) A second mass spectrometer has been also built. It includes a Bauer-Signer source, a 60° and 12.5 cm radius magnetic sector. It is designed to perform a second enrichment step with low Kr gas pressure released by vaporizing implanted Al layer during the first enrichment step.

- 4) A new facility based on resonance ionization spectroscopy – time of flight mass spectrometry (RIS-TOF) is now operating. It is capable to perform isotopic abundance measurements from samples containing only a few thousands atoms of Kr. Krypton ionization is done by resonant 2 + 1 UV photons at 216 nm. It includes also a cold trap to enhanced ionization efficiency. The design of the spectrometer is similar to RELAX instrument developed for Xe measurements by J. Gilmour [8] with an adjustment of the laser wavelength for Kr ionization.

One of the main issues of these new instruments is to measure ^{81}Kr concentrations for dating ice core for paleoclimatic reconstruction and ancient groundwater for modeling hydrogeologic systems. However the very high sensitivity of the RIS-TOF type instrument allows measurements of, fissionogenic, radiogenic and cosmogenic Kr concentrations to decipher thermal history and geochronology of minerals or to determine cosmic ray exposure of small meteorite samples.

Acknowledgements

The CNAB project was financially supported by ANDRA, by the Région Aquitaine (France), by CNRS (GdR FOR-PRO, Chemistry and SDU-INSU Departments), and by the University Bordeaux 1. Collaboration with N. Thonnard (Institute of Rare Isotope Measurement, Knoxville, University of Tennessee) was very fruitful.

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Development of krypton separation system for the application of ATTA in geochemistry

R. Yokochi, L. J. Heraty, N. C. Sturchio

*Department of Earth and Environmental Sciences, University of Illinois at Chicago
845 W. Taylor Street, Chicago, IL 60607-7059, U.S.A.*

Radiokrypton isotopes (^{81}Kr , $t_{1/2}=229,000$ years and ^{85}Kr , $t_{1/2}=10.8$ years) are ideal tracers of geochemical processes that involve atmospheric components (e.g. in groundwater, sea water, ice cores and the atmosphere, e.g. [1]). However, due to their low isotopic abundances ($\sim 10^{-12}$ for ^{81}Kr and $\sim 10^{-11}$ for ^{85}Kr) only ^{85}Kr has been conventionally measured by low level counting. The recent application of Atom Trap Trace Analysis (ATTA) on Kr at Argonne National Laboratory now enables the quantification of both ^{81}Kr and ^{85}Kr [2,3].

Atmospheric components contain a few ppm of krypton. As ATTA analyses currently require $\sim 50 \mu\text{L}$ of pure krypton, it needs to be purified from 50-100 L (at STP) of gas sample. The progress in development of the krypton separation procedure is reported herein.

Procedures and efficiency

Atmospheric components (atmosphere and gases extracted from air-saturated water) contain nitrogen (65-99 %), argon (1-2 %), oxygen (0-35 %) and a trace amount of

krypton (2.5 ppm at most). Additionally, natural samples can contain water vapour, carbon dioxide, hydrogen sulphide and methane. Figure 1 shows the outline of the process under development to separate these gases; (i) H_2O and CO_2 removal using adsorbents, (ii) cryogenic distillation for a rough separation of krypton from other major atmospheric gases, (iii) gas chromatography for complete Ar-Kr and CH_4 -Kr separation. A quadrupole mass spectrometer (RGA-200 by Stanford Instruments) is connected to the Kr separation line, and was used to examine the efficiency of gas separations.

At liquid nitrogen temperature, nitrogen, argon and oxygen have higher vapor pressures than krypton by factors of about 330, 100 and 110, respectively. Exploiting these physical property differences, the first stage of the purification is by cryogenic distillation. Sample gas (16 L tank, 5 bars) is condensed into a smaller container at liquid nitrogen temperature. Most of the condensation process occurs spontaneously within 5 minutes, and an additional 10 minutes' operation of a vacuum compressor condenses 98% of the total sample. The

gas phase in equilibrium with this condensed liquid should be depleted in krypton by a factor of a few hundred, thus the removal of this gas phase results in an enrichment of Kr in the residual liquid phase. During this process, the $\text{N}_2/^{40}\text{Ar}$ ratio of the gas phase is monitored to evaluate whether the ex-

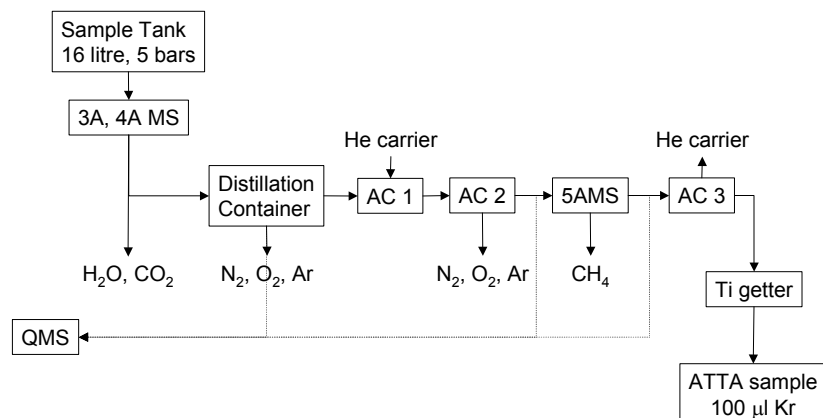


Figure 1: Flow chart of the Kr separation system. AC and MS represents activated charcoal and molecular sieve, respectively.

pected elemental fractionation actually takes place. Theoretically, the residual liquid (1-2 L at STP) is expected to represent a few percent of the initial sample while retaining 97% of the initial krypton inventory by the end of the distillation procedure. However, some of the processes do not occur in strict equilibrium, and the current estimate of the Kr yield through this procedure is >80% according to the observed $N_2/^{40}Ar$ ratios. The distillation residue is then entirely adsorbed on a cold activated charcoal trap (AC1). Subsequent packed column gas chromatography allows more complete purification. AC2 separates the residual nitrogen, oxygen and argon from krypton as shown in Figure 2. The molecular sieve 5A column (MS5A) selectively retains methane longer than krypton, which will be trapped at AC3 held at liquid nitrogen temperature.

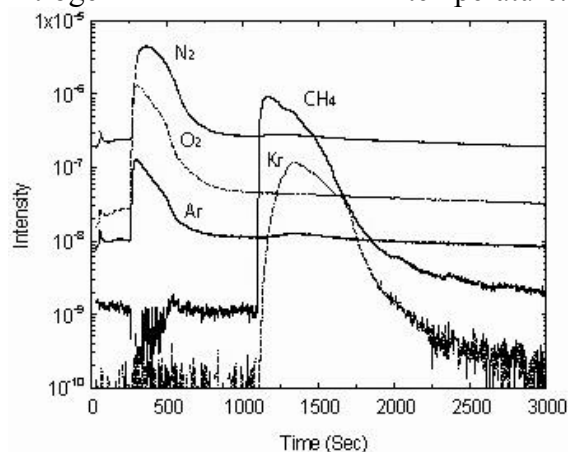


Figure 2: Results of gas chromatographic separation between $N_2/O_2/Ar$ and Kr by activated charcoal. Sample gas constitutes of 96 % air, 5% methane and 1% krypton. The quantity of gas used for this spectra was approximately 300ccSTP.

Finally, the carrier gas (He) is removed from the AC3 by pumping, and the trapped gas is subsequently desorbed and exposed to a hot titanium getter. Pure krypton is then collected in a sample cylinder containing activated charcoal held at liquid nitrogen temperature. Overall Kr yield of 70-80 % is expected through the entire separation process according to the available results.

Future developments

Chemical separation of H_2S is required before the distillation procedure to prevent vacuum line corrosion. This H_2S removal method is to be established before extending this procedure to high- H_2S samples.

Most of the valves in the purification line are air-actuated, and are controlled through the LabVIEW software, which will allow for future automation of the entire system. Temperature controls, gauges, and QMS software will be integrated to the LabVIEW system in the future.

Application to noble gas analysis

A complete separation of krypton from argon or xenon is a difficult task, while it is helpful for precise isotope analyses. It is possible to apply the above-mentioned gas chromatography separation for such purpose, to obtain large noble gas samples for high-precision mass spectrometry in dynamic mode, whereas a carrier gas-free procedure is desirable when dealing with small noble gas quantities. An attempt to separate noble gases by carrier-free chromatography is underway, and the uses and problems of this method may be discussed.

Acknowledgments

This work was supported by the Camille and Henry Dreyfus Postdoctoral Program in Environmental Chemistry and the National Science Foundation.

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New Developments in Atom-Trap Trace Analysis of ⁸¹Kr and ⁸⁵Kr

Y. Ding^{1,2}, K. Bailey², A. M. Davis^{3,4}, R. W. Dunford², S.-M. Hu², Z.-T. Lu^{1,2,3},
T. P. O'Connor², N. C. Sturchio⁵, L. Young⁶

¹Enrico Fermi Institute, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, U.S.A.

²Physics Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439 U.S.A.

³Dept. of Physics, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637 U.S.A.

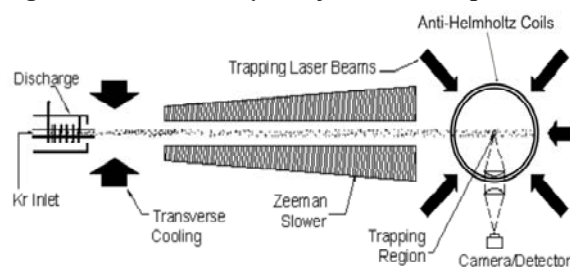
⁴Dept. of Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637 U.S.A.

⁵Dept. of Earth & Environmental Sciences, University of Illinois at Chicago, 845 W. Taylor Street,
Chicago, IL 60607, U.S.A.

⁶Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439 U.S.A.

Two radioactive isotopes of krypton (⁸¹Kr, $t_{1/2} = 229,000$ yr, and ⁸⁵Kr, $t_{1/2} = 10.8$ yr) are valuable environmental tracers having powerful applications such as determining groundwater residence times, ocean circulation and mixing rates, and ages of glacial ice. The analysis of these isotopes is now best accomplished by using the ultrasensitive Atom-Trap Trace Analysis (ATTA) apparatus developed at Argonne National Laboratory. This apparatus uses tuned diode lasers to hold and count individual Kr atoms with complete isotopic selectivity in a magneto-optical trap [1]. The atoms are first excited to a metastable state (Kr*) by using a RF-driven electron discharge, then Kr* atoms are collimated and trapped using 811-nm laser beams (Fig. 1).

Figure 1. Schematic layout of the atom-trap beam-



line of ATTA-2. Metastable krypton atoms (⁸¹Kr*) are produced in the discharge. The ⁸¹Kr* atoms are transversely cooled, slowed and trapped by the laser beams shown as solid arrows. The fluorescence of individual trapped ⁸¹Kr* atoms is imaged to a detector. Fine-tuning of the laser wavelength can select other Kr isotopes for trapping and detection. Total length of the apparatus is about 2.5 meters. From [2].

The detection method uses photon burst spectroscopy, whereby an atom can be trapped and observed for 100 ms or longer, during which 10^6 fluorescence photons can be induced from a single trapped atom and as many as 10^4 photons can be detected (Fig. 2).

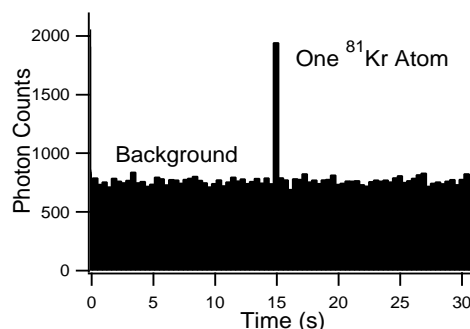


Figure 2. Signal of a single trapped ⁸¹Kr atom. The background is due to light scattered off vacuum-chamber walls. Single atom signal ~ 1600 photon counts, background ~ 340 photon counts. From [2].

The current version of the instrument, ATTA-2, has an overall efficiency of 10^{-4} and requires ~50 μ L of Kr per analysis of ⁸¹Kr, which is the amount contained in ~700 L of air-saturated water. By cross-calibration of ATTA-2 with low-level counting of ⁸⁵Kr, and by using a ⁸⁵Kr spike, it was found that pre-bomb and post-bomb atmospheric air samples have indistinguishable ⁸¹Kr/Kr ratios (within measurement error of $\pm 8\%$) [2]. Also, the mean residence time of groundwater from the

Nubian aquifer in the oasis areas of the Western Desert of Egypt was found to have a range of 2×10^5 to $\sim 1 \times 10^6$ yr [3].

Here we describe a new breakthrough in the optical excitation of Kr that will allow us to realize the completion of the next-generation instrument, ATTA-3, having a major improvement in efficiency leading to a 100-fold reduction in sample size. This reduction in sample size may help make ATTA a routine geochemical tool within the next decade.

New Excitation Method

Due to the lack of a cw, narrow-bandwidth laser at 124 nm, laser trapping of krypton atoms can only be realized with atoms at the metastable $5s[3/2]_2^0$ level (Fig. 3). In ATTA-2, the excitation of Kr atoms to the metastable level is done by colliding atoms and electrons in a plasma discharge, which poses a serious limitation to the analyzer. The discharge source has a low excitation efficiency ($Kr^*/Kr \sim 10^{-4}$); the collision process causes the atomic beam to diverge; in the plasma, Kr^+ ions are slowly imbedded into surfaces, causing a loss of sample, only to re-emerge later in subsequent analyses, and thereby inducing cross-sample contamination; moreover, a discharge requires a certain minimum gas pressure to operate, which raises the minimum amount of sample needed to support the operation of the discharge.

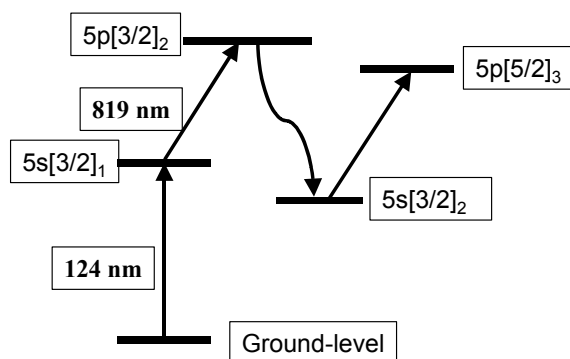


Figure 3. Atomic energy diagram of Kr. The new optical excitation scheme (124 nm + 819 nm) is shown. From [5].

In order to avoid these problems and improve both the atom counting rate and

counting efficiency, we have been investigating alternative sources of metastable Kr^* atoms. It had been previously demonstrated that Kr atoms can be transferred from the ground level to the metastable level via a two-photon excitation process (Fig. 3): excitation with a vacuum ultraviolet photon at 124 nm and an infrared photon at 819 nm, followed by a spontaneous decay at 760 nm [4]. All three transitions are of the allowed E1 type. Based on this scheme, we have recently realized, for the first time, a beam of metastable Kr^* atoms produced by photon excitation [5]. In the experiment, a vacuum ultraviolet Kr lamp was used to generate the 124 nm photons that are resonant with Kr atoms at the ground level. The 819 nm light was supplied by a Ti:sapphire ring laser system. At the optimum lamp and laser conditions, the metastable Kr^* beam has reached a flux comparable to that produced with a RF-discharge in ATTA-2. With better engineering controls such as a liquid-nitrogen-cooled Kr atom source and a longer optical excitation path, we believe that a higher Kr^* beam intensity can be reached. This optical production scheme is a clean and efficient way of producing a well-collimated beam of metastable Kr^* atoms, and will enable the analysis of smaller sample sizes required by many geochemical and cosmochemical applications.

Acknowledgments

Supported by the U. S. Dept. of Energy's Office of Nuclear Physics and a University of Chicago-Argonne National Laboratory Collaborative Research Seed Grant.

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Precise measurement of atmospheric helium isotopes

Y. Sano¹, T. Tokutake¹, N. Takahata¹

¹ Center for Advanced Marine Research, Ocean Research Institute, The University of Tokyo, Minamidai 1-15-1, Nakano-ku, Tokyo 164-8639, Japan

Introduction

Since the mixing time of atmospheric helium is significantly short compared to the residence time, the air ³He/⁴He ratio has been considered to be uniform on a global scale. Mamyrin et al. [1] reported that the atmospheric ³He/⁴He ratio did not vary with latitude, longitude, and altitude (up to 10 km) within the error margins of the individual measurements of about 5%. Sano et al. [2] measured the ³He/⁴He ratio of air samples collected over a 10-year period at various sites in Japan and claimed an apparent 1-2% decrease in the ratio. They attributed the decrease to the anthropogenic release of crustal ⁴He, even though they admitted an experimental artifact. If the change of atmospheric ³He/⁴He ratio with time is the case, it has serious implications for helium isotope geochemistry, since the most laboratories use air helium as laboratory standard.

In a Comment on the paper [2], Lupton and Graham [3] reported a slope of $+0.009 \pm 0.043$ %/year (2σ) for the time rate of atmospheric ³He/⁴He change (TROC) based on the Pacific marine air collected over a 17-year period. In contrast, Sano [4] suggested a TROC of -0.033 %/year, which was compatible with the estimates of anthropogenic addition of radiogenic helium. Pierson-Wickman et al. [5] measured ³He/⁴He ratios of helium trapped in historical metallurgical slags in an attempt to study the secular variation of the ratio. Taking into account of data, they proposed a TROC of -0.014 ± 0.007 %/year. Recently Lupton and Evans [6] reported that a TROC could be between -0.0102 and $+0.0019$ %/year, which corresponds to a 0.3% decrease at the most in the atmos-

pheric ³He/⁴He over the past 3 decades. They claimed that the TROC is below the detection limit of most laboratories.

Even though many efforts have been devoted to the secular variation of air helium as described above, the change of atmospheric ³He/⁴He ratio with latitude and longitude have not been assessed since the pioneer work of Mamyrin et al. [1]. We develop an analytical system to measure atmospheric ³He/⁴He ratio at about 0.2% error margin (2σ) and will apply the method to air samples collected various sites in Japan and Taiwan.

Experimental

A lead glass container equipped with two vacuum valves at both ends was evacuated using a rotary pump with liquid nitrogen trap down to 1×10^{-3} Torr. At the sampling site, both valve were opened and air sample was collected up to atmospheric pressure. After a few minutes to wait an equilibrium, both valves were closed.

About 0.1 cm³STP of each air sample was admitted into the vacuum line described by Sano and Wakita [7] with some modification where helium and neon were separated from the other gases by activated charcoal traps kept at liquid nitrogen temperature and hot titanium getters. The ⁴He/²⁰Ne ratio was determined by on-line quadrupole mass spectrometer (Prisma80, Pfeiffer Vacuum). Helium was then separated from neon by a cryogenic charcoal trap kept at 40 K and transferred into a high precision helium isotope mass spectrometer (Helix SFT, GV instruments). The ³He⁺ and ⁴He⁺ beams were measured simultaneously by double collector system. The intensity of ³He⁺ beam was detected

by an ion counting system equipped with a secondary electron multiplier at the mass resolving power of about 700 while that of $^4\text{He}^+$ was by a Faraday cup at the power of about 400. We use the new internal helium standard of Japan (HESJ) prepared by Matsuda et al. [8] as a running standard to calibrate the atmospheric $^3\text{He}/^4\text{He}$ ratio. Known amount of HESJ, 2.0×10^{-7} ccSTP was admitted into the mass spectrometer and sensitivity of helium was assessed. Observed sensitivity was about 4×10^{-4} A/Torr at the trap current = 800 μ A, which is four times better than that of VG5400 [7].

Results and Discussion

Generally there is a pressure effect in a static vacuum mass spectrometer. In the case of VG5400, the pressure dependence of the $^3\text{He}/^4\text{He}$ ratio was up to 6% with the sample size variation of one order of magnitude [7]. Higher the total pressure, the lower the $^3\text{He}/^4\text{He}$ ratio was observed. There is also pressure effect in Helix SFT. However the trend is contrary and the discrimination is up to 2% in this study. Thus it is necessary to balance the amounts of sample and standard. Reproducibility of $^3\text{He}/^4\text{He}$ ratios of HESJ sample was checked by repeated measurements within successive six days. Single analysis shows the error of 0.1~0.2% (2σ), while the average of 17 measurements indicates the error of 0.03% (2σ) where one take into account the error weighted mean. When we measure air sample, we adopt $A_1 B_1 A_2 B_2 A_3$ method where A and B denote HESJ standard and air helium, respectively. Observed $^3\text{He}/^4\text{He}$ ratio of sample B_1 is calibrated against the average of A_1 and A_2 . Error of B_1 analysis is calculated as taking into account of B_1 itself as well as A_1 and A_2 in quadrature.

We have measured air samples collected at a small park close to our campus in Nakano, Tokyo. When we take the error weighted mean of nine successive analysis, the average of HESJ is $20.405 \pm 0.040 R_{\text{air}}$ (2σ) where R_{air} is the $^3\text{He}/^4\text{He}$ ratio of the Nakano air. Matsuda et al. [8] compiled

the $^3\text{He}/^4\text{He}$ data of HESJ (expressed as R/R_{air}) reported by four laboratories in Japan. They recommended that the value of HESJ is $20.63 \pm 0.10 R_{\text{air}}$ (2σ). Lupton and Evans [6] reported the HESJ value of $20.408 \pm 0.044 R_{\text{air}}$ (2σ). Our value of $20.405 \pm 0.040 R_{\text{air}}$ agrees well with that of Lupton and Evans, but significantly lower than the recommended value. Lupton and Evans concluded that either a) their HESJ sample was fractionated in comparison to the other HESJ, or b) their air standard has a higher $^3\text{He}/^4\text{He}$ ratio than those in some Japanese laboratories. If the latter is the case, atmospheric $^3\text{He}/^4\text{He}$ ratio may vary with latitude and longitude. We are now measuring the $^3\text{He}/^4\text{He}$ ratio of air samples collected various sites in Japan and Taiwan and will present the data at Conference.

Acknowledgments

We thank T.F. Yang, D. Pinti for assistance in collection of air samples. This work was partly supported by the Grant-in-Aid for Scientific Research Program No. 17101001 from Ministry of Education, Science and Culture of Japan.

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Atom-Trap-Trace-Analysis (ATTA)

Heiner Daerr, Markus Kohler and Martin Kalinowski

Carl-Friedrich von Weizsäcker Zentrum für Naturwissenschaft und Friedensforschung (ZNF), Hamburg, Germany

Atom trap trace analysis (ATTA) [1] is a new and advanced technique for the detection of very rare tracers. This project focuses on the detection of two rare krypton isotopes (^{81}Kr and ^{85}Kr).

The difference in transition frequencies due to isotope shift and hyperfine splitting (several 10MHz up to GHz) is used to distinguish, using optical excitation, between the different isotopes. The smearing of the optical fingerprint caused by the Doppler effect at room temperature can be eliminated by laser-cooling and adjacent magneto-optical trapping.

Possible applications are groundwater dating, measurement of underground oil streams or, for our purpose, verification of the "Non proliferation treaty (NPT)".

The poster gives a short review of past ATTA experiments and our preparation for future research at the ZNF in Hamburg.

Acknowledgments

This work is supported by the German Foundation for Peace Research (DSF) and we are grateful to Prof. Klaus Sengstock for scientific support on atom traps.

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Simultaneous determination of noble gases, N₂, O₂, SF₆, CFC-11 and CFC-12 in water by GC-MS/ECD

Markus Hofer¹ and Rolf Kipfer^{1,2}

¹ *Eawag: Swiss Federal Institute of Aquatic Science and Technology, CH 8600 Duebendorf, Switzerland.*

² *Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, CH 8092 Zurich, Switzerland.*

Introduction

SF₆ and CFCs are widely used as natural tracers for water dating. Especially SF₆ is sensitive to excess air and infiltration temperature which both have to be known and corrected for in order to obtain reliable dating results. Although excess air and infiltration temperature can be calculated from noble gas concentrations, separate measurements of SF₆, CFCs and noble gases are laborious and cost intensive. With this in mind we developed a method to measure all these compounds simultaneously from one water sample.

Sampling and Extraction

Water samples are collected without air contact into 500 cc stainless steel cylinders (Whitey, 304L-HDF4-500, Arbor Inc.) equipped with two ball valves (Whitey, SS-43GM4-S4, Arbor Inc).

The gases are quantitatively extracted from the water (>99%) by vacuum extraction for 30 min. Water vapor is freed out on a first cold trap at -196°C. The CFCs are retained on a second trap at -140°C and Ne, Ar, Kr, Xe, N₂, O₂ and SF₆ are adsorbed on a third trap filled with 2 g of molecular sieve 5Å (Merck Inc.) at -196°C. He and an aliquot of Ne remain in the gas phase. After extraction the purified gases are transferred sequentially from the traps to the analytical part of the device.

Measurement

The gases Ne, Ar, Kr, Xe, N₂ and O₂ are injected afterwards to the gas chromatograph

(Finnigan TraceGC ultra, Thermo Inc.) through a 1 cc gas sampling loop and are separated on a 4 m x 0.32 mm Carboxen 1010 Plot Capillary Column (Supelco Inc.) followed by a 30 m x 0.32 mm x 25 µm HP-Molsiv column. The carrier gas is He at 1.5 cc/min with a split ratio of 75. The noble gases are quantified using a quadrupole mass spectrometer (Finnigan TraceDSQ, Thermo Inc.).

SF₆ and CFCs are injected simultaneously through a second sampling loop to the GC and are separated on a 60 m x 0.32 mm GS-Gaspro capillary column (J&W Scientific) and quantified on an Electron Capture Detector (Thermo Inc.). The carrier gas is He at 12 cc/min with a split ratio of 8 and a makeup gas flow of 30 cc/min N₂. The GC oven is temperature programmed from 40°C to 220°C.

He and an aliquot of the Ne are measured statically using a RGA 100 quadrupole mass spectrometer (Stanford Research Systems).

Conclusion

First measurements of water samples from Lake Lugano show very promising results and give an idea of the potential of this method.

Acknowledgments

We are grateful for support to Nora Graser, Urs Menet, Philippe Perisset, Christian Ehrat and Heiri Baur.

Method for Extraction of Dissolved Gases From Groundwater for Radiokrypton Analysis

P. C. Probst, R. Yokochi, N. C. Sturchio

*Department of Earth and Environmental Sciences, University of Illinois at Chicago
845 W. Taylor Street, Chicago, IL 60607-7059, U.S.A.*

Two radioactive isotopes of krypton (Kr) are valuable environmental tracers having powerful applications such as determining groundwater residence times, ocean circulation and mixing rates, and ages of glacial ice. ^{81}Kr ($t_{1/2} = 229,000$ yr) is an ideal tracer on the 10^4 to 10^6 year time scale. ^{85}Kr ($t_{1/2} = 10.8$ yr) is ideal for tracing processes in the <50 yr range. The isotopic analysis uses the Atom Trap Trace Analysis (ATTA) apparatus developed by Z.-T. Lu and colleagues at Argonne National Laboratory. This apparatus uses tuned diode lasers to hold and count individual Kr atoms with complete isotopic selectivity in a magneto-optical trap ((Chen et al., 1999; Du et al. 2003). ATTA analysis currently requires ~ 50 μL of Kr, which is the amount contained in ~ 700 L of air-saturated water. The object of this $^{81}\text{Kr}/\text{Kr}$ analysis has recently dated groundwater from a Nubian aquifer in the Western Desert of Egypt to be as old as 106 years. The results of the ATTA analysis showed agreement to ^{36}Cl data and marked the first time ATTA was used to determine groundwater residence time (Sturchio et al., 2004). We developed a new, high-volume gas-extraction system, EDGAR (Extraction of Dissolved Gases for Analysis of Radiokrypton) that provides a simple and rapid method for obtaining high-volume samples suitable for recovery of micromolar amounts of non-reactive trace gases for isotopic analysis.

Method

The key component of EDGAR is a hydrophobic semi-permeable membrane contactor (Membrana Corp.). This extracts dis-

solved gases from water with efficiency approaching 90%. Water flows through the inner surface of the membrane and a vacuum is applied to the outer surface of the membrane. Vacuum is produced with the compressor that compresses the extracted gas into a standard gas cylinder. The extraction apparatus is contained in a rigid frame (Fig.1). EDGAR weighs about 180 kg and is powered by a 120VAC, 20-amp power source. Electronic sensors monitor the membrane vacuum, sample tank pressure, water temperature and total water flow. A data logger records the sensor signals. A schematic of EDGAR is shown in Fig. 2.



Figure 1. Picture of EDGAR being deployed in the field.

Testing

Initial testing of membrane extraction efficiency was conducted using Chicago tap water. Dissolved O_2 (DO) was measured in water before and after passing through the membrane at flow rates ranging from 4 to 34 L/min. DO dropped from 12 to 15 mg/L (before) to 1.6 to 3.7 mg/L (after),

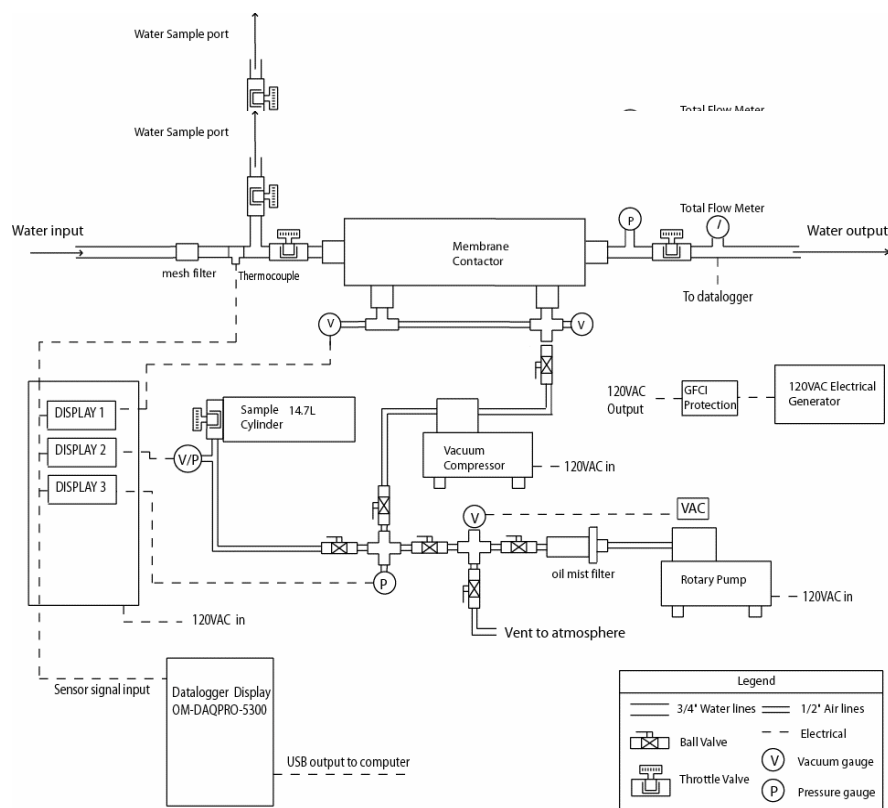


Figure 2. Schematic diagram of EDGAR.

indicating DO extraction efficiency of 67 to 88 % at a flow rate of 4 to 5 L/min. The DO extraction efficiency decreased with membrane vacuum pressure and with flow rate (Fig. 3), but was insensitive to water pressure in the range 1,000 to 3,000 torr.

Field testing of EDGAR was performed on a groundwater well in Oswego, IL. The compositions of dissolved and extracted gases were measured using a quadrupole mass spectrometer. The concentration of O₂ was at blank level in these samples, indicating negligible atmospheric contamination. Nitrogen in extracted gas was enriched by ~15 % and Kr was depleted by ~21 % relative to Ar. The correlation between DO extraction efficiency (E_{ox}) and membrane vacuum pressure suggests that water and gas phases across the membrane are in solubility equilibrium. Consequently, extraction efficiencies of other gas species *i* (E_{*i*}) can be estimated as a function of their solubilities (S_{*i*}) from:

$$\frac{S_i E_i}{(1 - E_i)} = \frac{S_{ox} E_{ox}}{(1 - E_{ox})}$$

According to this model, E_{*i*} values for N₂, CH₄, Ar, and Kr are expected to be 0.89, 0.78, 0.78 and 0.65 respectively for E_{ox} = 0.8 at ambient temperature (0 to 20°C). Nitrogen and Kr should then be fractionated relative to Ar by +14% and -17%, respectively, which is roughly in agreement with the observation. E_{*i*} values for Ar and O₂ are nearly equal.

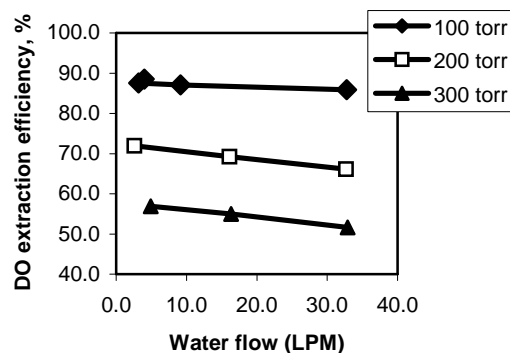


Figure 3. DO extraction efficiency (%) vs. water flow rate as a function of pressure on the gas side of the membrane.

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This work was supported by the National Science Foundation.

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Measurements of helium concentration in groundwater using gas chromatographic method

J. Pusz, I. Śliwka, J. Lasa

The Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Science

Radzikowskiego Str. 152, 31-342 Kraków, Poland

Gas chromatography (GC) measurements of helium [1] can be used as an alternative to mass spectrometry (MS) determinations of ⁴He for groundwater dating.

A scheme of the measurement system developed in the Institute of Nuclear Physics in Cracow is presented in Figure 1. The system consists of a gas chromatograph equipped with a Valco TCD detector of 2μl volume; 10 port valve V10; three chromatographic columns K1 (1.5 m), K2 (7 m) and K3 (2 m); sample loop V_p; system of helium enrichment and the vacuum pump, P. As a carrier gas argon 6.0 is used. Water samples are taken to the stainless steel containers of volume 2900 cm³. Helium is extracted from water samples by the head-space (HS) method [2,3]. The HS gas of volume V = 200 cm³ passes through a system of two (vacuumed earlier) traps, T1 and T2 immersed in liquid nitrogen, D. In the first trap T1, the water vapour is stopped. In the second trap T2 filled with activated charcoal, oxygen and nitrogen are adsorbed whereas helium and neon are not adsorbed and fill the volume of the sample loop V_p, the trap T2 and a pipe connections (also earlier vacuumed). After changing the position of V10, helium and neon from sample loop are dosed to the first column K1 (filled with molecular sieve 5A) [4]. When helium and neon gets to the second column K2 (also filled with molecular sieve 5A), the position of V10 is changed back and the compounds which remained in the column K1 are removed from the system. The columns K1 and K2 are working in the “back flush” mode. For a better separation, both gases (i.e. helium and neon) pass through the third column K3 (filled with a mixture of molecular sieve 5A and

activated charcoal 50%/50%) to the TCD detector. The signal from the detector is registered in a computer equipped with appropriate software.

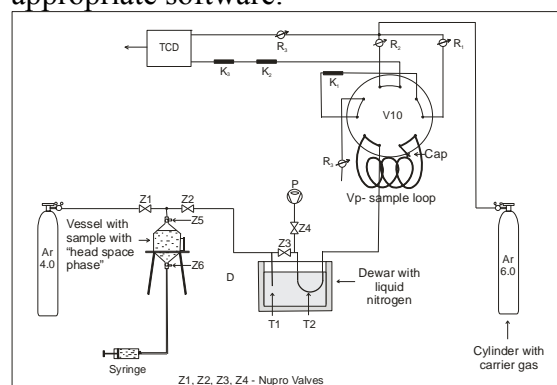


Fig. 1. Scheme of the chromatographic system measuring helium concentration in groundwater.

Examples of the chromatograms of the helium concentration analysis in air, surface water and groundwater obtained through the chromatographic method described above are shown in Figs 2, 3, 4 and 5, respectively. Figure 6 shows the results of calibration of the system with the standard 101±5 ppm helium in argon (produced by Linde Gas).

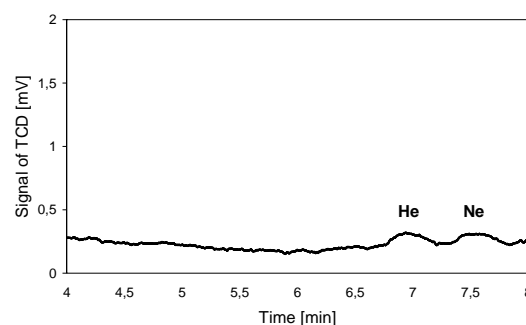


Fig. 2. The chromatogram of helium concentration analysis in 10 cm³ of air without the system of enrichment (LOD of TCD: 2.8 ng He).

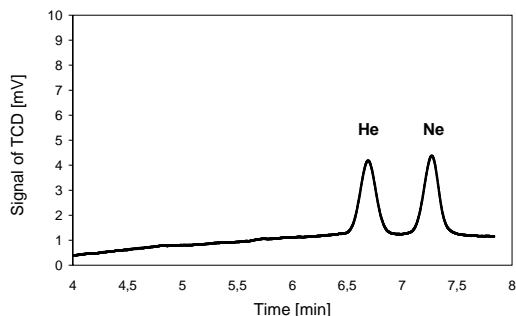


Fig. 3. The chromatogram of helium concentration analysis in 200 cm³ of air with the system of enrichment.

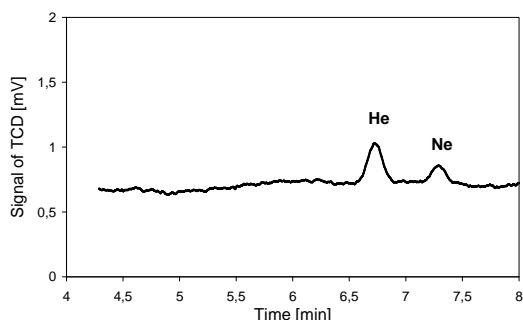


Fig. 4. The chromatogram of helium concentration analysis in surface water with the system of enrichment.

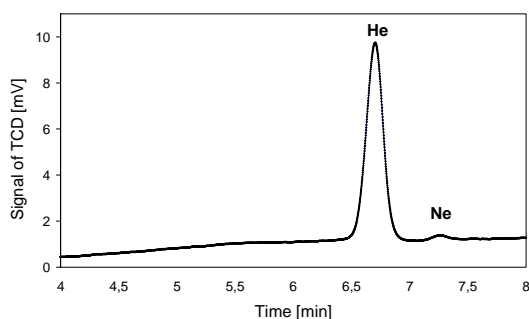


Fig. 5. The chromatogram of helium concentration analysis in groundwater of glacial age in Cracow with the system of enrichment.

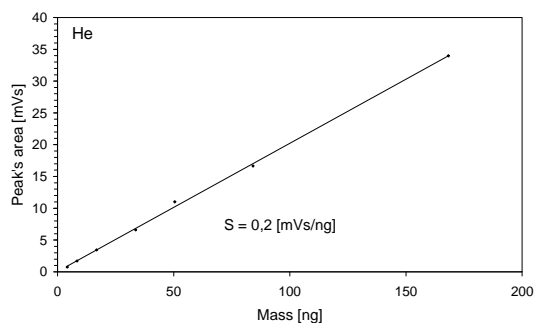


Fig. 6 The results of the calibration of the TCD detector, (1 ng = 560·10⁻⁸ cm³ STP).

Examples of comparisons of He analyses performed with the aid of GC system with those performed earlier by MS technique in water of glacial age in the Cracow area are shown in Table 1.

Table 1. Helium in 10⁻⁸ cm³STP/g measured by MS in 1992 [5] with uncertainty lower than 4%, and by GC in 2006.

Well	⁴ He (MS)	He (GC)
11	185	184±5
15	212	225±6
16	225	240±7

In the Busko area, southern Poland, mineral waters of interglacial age occur with ⁴He_{exc} of (12000 to 15400)·10⁻⁸ cm³STP /g [6]. Similar water was found in a recently drilled well about 10 km SE of Busko with He content of (9500)·10⁻⁸ cm³STP/g as determined with the aid of GC technique.

In conclusion, the developed system can be regarded as suitable for helium determinations in groundwater for dating purposes.

Acknowledgments

This work was partly supported by grants No. 4T12B 004 28 and 3T09D 038 29 from the Ministry of Sciences and Education.

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The GFZ Noble Gas Lab: Equipment and Recent Research

S. Niedermann¹, N.A. Stroncik¹, J. Lippmann-Pipke^{1,2}, C.R. Fenton¹,
M. Goethals¹, T. Krüsmann¹, T. Wiersberg¹, E. Schnabel¹ and J. Erzinger¹

¹GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

²Institute for Interdisciplinary Isotope Research IIF Leipzig, Permoserstr. 15, D-04318 Leipzig, Germany

Here we would like to present the noble gas laboratory at GeoForschungsZentrum Potsdam, the hosting institution of MI-NOGA 2007, to its participants.

Equipment

There are two complete noble gas lines which are both used for the whole spectrum of noble gases, from He to Xe. Each line comprises an ultrahigh vacuum extraction furnace, a purification line, a cryogenic adsorber system, and a VG5400 noble gas mass spectrometer. In the resistance furnaces, rock samples up to ~2 g in size can be heated to a maximum of 2000°C in a Ta crucible with Mo liner using heating elements made of graphite. Extracted gases are admitted to the purification line, where in a first step water is frozen to a dry ice-cooled trap, and subsequently the remaining chemically active gases are removed by two Ti sponge and two SAES (ZrAl) getters. The cryogenic adsorbers, which are used for separation of different noble gases from each other, look a bit different on the two lines. One is equipped with two cold heads containing a stainless steel frit for adsorption of Ar, Kr and Xe at 50 K and activated charcoal for He and Ne adsorption at 11K, respectively, whereas the other one contains a charcoal finger only but can be heated up to 400 K for complete Xe release from the charcoal. In both cases the cold heads are sequentially heated after complete noble gas adsorption in order to allow individual admission of each noble gas to the mass spectrometer.

In addition to the furnace, one line includes an ultrahigh vacuum crusher, where miner-

als or glasses are crushed between two hard-metal jaws to mechanically extract gases from grain boundaries, fluid inclusions or vesicles. The other system comprises a water degassing line, which allows the separation of a gas phase from the water by ultrasonic agitation and making use of a laminar gas flow through a capillary to a liquid nitrogen-cooled trap. Gas samples can also be attached to this line and suitable volume splits can be admitted to the purification line for further treatment as described above.

Mantle Geochemistry

The predominant part of research done in the GFZ noble gas lab is based on measurements of rocks, with one of the two main research fields being mantle geochemistry. He and Ne isotopic and abundance studies of mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) have provided important insights into the formation, evolution and composition of the Earth's mantle. Basic concepts on mantle structure and evolution (e.g. "layered mantle models") are primarily based on the interpretation that mantle ³He and ²²Ne reflect primordial, undegassed mantle material, with deviations from primordial isotope signatures having increased during Earth's history due to the production of radiogenic ⁴He and nucleogenic ²¹Ne, which are both related to U and Th decay [e.g. 1]. Mantle He and Ne isotopic ratios are thus controlled by the ratios of [primordial ³He]/[U+Th] and [primordial Ne]/[U+Th], respectively.

However, OIBs from individual mantle plumes, such as Hawaii, Easter or Foundation, display a distinct isotopic variability, which is probably related to mixing processes in the mantle and thus interpreted in terms of sampling different mantle reservoirs. Little is known about the contribution of magmatic processes in mantle plumes to those heterogeneities. Without an understanding of these processes and their contribution to geochemical tracers it is difficult to accurately explain the composition and evolution of the Earth's mantle. Thus our current projects are concerned with the detailed study of the noble gas isotope compositions of fresh, submarine and subaerial basaltic rocks from the Hawaii, Easter and Foundation plumes in order to resolve (1) the spatial and temporal distribution of plume material, (2) the magmatic and mantle dynamic processes in the plumes and (3) the compositions and developments of their mantle sources. Up to now the following results have been derived:

- He isotopes in olivine separates of subaerial Mauna Kea lavas from the Hawaii Scientific Drilling Project show an evolution towards higher $^3\text{He}/^4\text{He}$ with age [2] confirming earlier studies [3].
- Submarine Mauna Kea lavas erupted during the main shield-building stage show a spike-like pattern of high $^3\text{He}/^4\text{He}$ between ~ 12 and $23 R_A$ [2, 4].
- The Ne isotopic signature shows no depth dependence in the drill core, remaining plume-like over the whole length of the Mauna Kea and Mauna Loa sections of the borehole [2].
- He isotope data obtained from fresh, submarine glasses of the Easter Microplate (EMP)–Easter Seamount Chain (ESC) ($26 R_A$) and the Pacific-Antarctic-Rise (PAR)–Foundation Seamount Chain (FSC) system ($12 R_A$) establish that the plumes feeding those chains belong to the group of high ^3He plumes, comparable to Galápagos and Iceland [5].
- Ne isotope data of glasses from the ESC belong, similar to data from Iceland [6], to the most primitive Ne data obtained from a

hotspot setting today. This indicates that the solar Ne component within the Earth's mantle may have survived virtually unchanged throughout Earth's history and that the He-Ne isotopic systematics can be decoupled, since the primitive Ne coincides with non-solar $^3\text{He}/^4\text{He}$ ratios [5].

- For the first time, coupled He, Ne and Ar isotope and relative abundance data from the EMP-ESC and PAR-FSC systems establish from a geochemical point of view that source material mixing in plume-ridge settings occurs in the physical state of melts and not in the form of solids or solid-melts.
- He, Ne and Ar fusion data from fresh, submarine volcanic glasses of a number of Mid-Atlantic Ridge off-axis seamounts show that He isotopes can be susceptible to interferences during melt formation and evolution resulting in a decoupling of He from Ne [6]: All obtained He data are indistinguishable from the MORB range, while Ne isotopic compositions show a clear plume signature.

Surface Exposure Dating

The second major focus of our research is connected to the method of surface exposure dating, which is based on the interaction of high-energetic cosmic ray particles with rocks on the terrestrial surface. In such interactions, nuclear reactions produce a variety of “cosmogenic” nuclides, among which a few long-lived radionuclides and rare noble gas isotopes (^3He , ^{21}Ne) can be used to investigate various processes shaping the Earth's surface [e.g. 8,9]. The main recent activities of our group within this field include:

Age of a coastal terrace in Asturias: Along the western Asturian coast of northern Spain, an up to 3-km-wide marine terrace extends for ~ 100 km and reaches an elevation of up to 100 m. It was formed as a wave-cut platform below sea level and was later uplifted, but both the time when it formed and the rate of uplift have been unknown. We have compared the concentrations of cosmogenic ^{21}Ne in quartzitic bedrock samples with those of ^{10}Be and

^{26}Al in order to deduce the history of that terrace. Exposure ages calculated from the three nuclides differ considerably, indicating that the terrace had a complex exposure history involving periods of burial by sediment or water. It was most probably formed during the Pliocene or early Pleistocene, and maximum uplift rates are 0.1-0.2 mm/a [10].

Production rate of cosmogenic ^{38}Ar : In addition to ^3He and ^{21}Ne , ^{38}Ar may be another noble gas isotope suitable for surface exposure dating. However, the production rate of cosmogenic ^{38}Ar in terrestrial surface rocks has not been known so far. We have measured He, Ne and Ar in pyroxene samples separated from Ferrar dolerite boulders that were exposed in the Antarctic Dry Valleys for up to several Ma. Since Ca is the only relevant target element for production of cosmogenic ^{38}Ar in these minerals, we were able to deduce the ^{38}Ar production rate from Ca based on their ^3He and ^{21}Ne exposure ages, resulting in a value of $\sim 220 \text{ at}/(\text{g Ca})^{-1} \text{ a}^{-1}$ [11].

Exhumation history of Southern Africa: High-elevation passive margins and their associated escarpments are the most prominent landforms resulting from continental break-up in Southern Africa. Using apatite fission-track (AFT) analysis combined with cosmogenic nuclide dating, we hope to track the long-term denudation history of various portions of Southern Africa's highlands. Our preliminary results indicate much lower rates of denudation in Late Cenozoic to recent times as compared to certain periods in the Mesozoic to Early Cenozoic. They provide estimates of vertical denudation rates between 0.5 and 3 m/Ma on the interior plateau and ~ 8 m/Ma along the margin of the escarpment.

CRONUS-EU: The ultimate goal of this EU-funded project (Cosmic-ray-produced nuclide systematics on Earth – The European contribution) is the development of an internationally accepted protocol allowing age determinations with accuracies better than 5%, rather than the 10-20% achievable at present. The GFZ contribution involves the determination of ^3He and ^{21}Ne

production rates in olivines from Ar/Ar-dated lava flows in the Grand Canyon area (Arizona, USA) as well as the comparison of production rates of several cosmogenic nuclides in various minerals suitable for surface exposure dating, such as olivine, pyroxene, quartz and magnetite. For the latter purpose we have sampled landslides in Argentina and Norway and the non-basaltic volcanic flow of Bishop Tuff (California, USA). First results will be presented at the EGU meeting in Vienna (April 2007).

Hydrology: Specialization on deep crustal fluids and gas samples

The third scientific focus of the lab concerns noble gas isotope investigations applied to deep crustal fluids and drill mud gas samples.

- A prominent recent result of *drill mud gas analysis* is the disclosure on the origin and spatial distribution of fluids at seismogenic depths of the San Andreas Fault [12]. In that study, Ne/Ar ratios have been used to identify the source of the atmospheric contribution, which is generally abundant in drill mud gas. Besides atmospheric Ne and Ar isotopic compositions, the samples show Ne/Ar ratios indistinguishable from air with no evidence for the contribution of an air-saturated water source. Hence, air correction of the measured $^3\text{He}/^4\text{He}$ ratios was performed using the measured ^{20}Ne concentration and the $^4\text{He}/^{20}\text{Ne}$ ratio of air (0.319). The air-corrected $^3\text{He}/^4\text{He}$ ratios fall between 0.2 R_A and 0.9 R_A and clearly differ between the Pacific Plate and the North American Plate. Whereas at most $\sim 5\%$ of the helium on the Pacific Plate is derived from the mantle, the contribution of mantle-derived helium reaches 10-12% on the North American Plate and increases with greater distance from the fault core. However, the overall contribution of mantle-derived helium to the total helium inventory of the San Andreas Fault is relatively low. We conclude that other, more permeable faults situated on the North American Plate act as main conduits for mantle-derived fluids.

- Results of the investigations of *deep crustal fluids* by means of noble gas analysis have been published shortly after the final installation of a quantitative water degassing line in the lab [13,14]. The most prominent result is related to the model age determination of ultra-deep fracture water in a South African mine. On the one hand, the study of the inert gases has shown that the Mponeng water has been isolated from the surface for about 20 Ma; on the other hand that water has been demonstrated to host life forms which are independent from the energy of the sun [15]: The bacteria exist without the benefit of photosynthesis by harvesting the energy of natural radioactivity to create food for themselves. The discovery of a stable, light-independent life form raises hopes of finding similar creatures on other planets.

Acknowledgement

For the above mentioned research projects funding has been provided by the Deutsche Forschungsgemeinschaft, the European Union and the GFZ Potsdam.

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Session 6:

Combining other tracers with noble gases

Interpretation of multi-tracer data sets, best practice recommendations, etc.

Multi-tracer data and groundwater modelling from modern to glacial ages: a case study in southern Poland

J. Kania¹ P. Mochalski², R. Purtschert³, K. Rozanski¹, S. Witczak¹, A. Zuber⁴

¹ AGH University of Science and Technology, Al. Mickiewicza 30, PL-30059 Krakow, Poland

² Institute of Nuclear Physics, Polish Academy of Sciences, ul. Radzikowskiego 152, PL-31342 Krakow, Poland

³ Institute of Physics, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland

⁴ Polish Geological Institute, Carpathian Branch, ul. Skrzatow 1, PL-31560 Krakow, Poland

Environmental tracers, including noble gases, are powerful tools for quantifying timescales of groundwater flow. They are also often employed in the process of calibration and/or validation of numerical flow and transport models.

The Bogucice Sands aquifer, southern Poland (Fig. 1) was investigated under EU research project [1]. It constitutes a typical Tertiary structure of deltaic origin, recharged at the outcrops in the south and discharged by upward seepage through the confining cover to Pleistocene sands in the north. Multi-tracer approach involving ³H, ³He, ⁴He, ⁸⁵Kr, CFCs, SF₆, δ¹⁸O, δ²H, δ¹³C, ¹⁴C, ³⁷Ar and ³⁹Ar was used to determine groundwater ages by lumped-parameter modelling and to improve the numerical flow and transport models of the system. Heavy noble gases measured by gas-chromatography and mass-spectrometry provided noble gas temperatures (NGT) for selected wells. Among 35 wells sampled for hydrochemistry, 25 were sampled for selected tracers and 15 were repeatedly sampled over the period of several years, mainly for ³H.

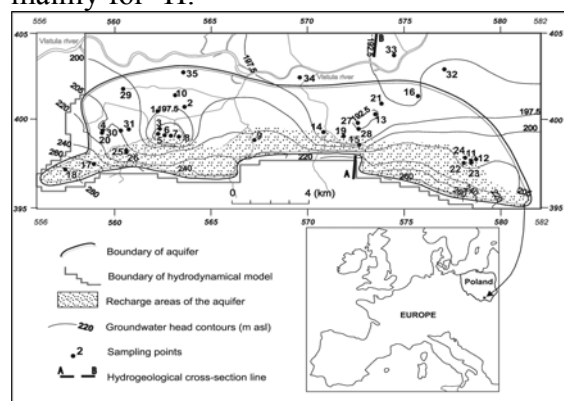


Fig. 1. Simplified hydrogeological map of the investigated groundwater system [2].

The results of tracer study and modelling focussing on the aquifer zone occupied by modern waters were reported in [2, 3, 4]. Within the present work, preliminary results obtained for the zones occupied by pre-modern waters are presented. Some findings from the earlier work are also recalled, especially in comparison with determinations of ⁸⁵Kr content and ³H/³He ratio in some wells.

Spatial distributions of ³H and ¹⁴C shown in Fig. 2 allow qualitative assessment of the timescales characterising the studied aquifer. It is apparent that while ³H distribution is strongly influenced by abstraction wells in and close to the recharge area, the ¹⁴C distribution still maintains natural pattern, with gradually decreasing ¹⁴C content towards the discharge area.

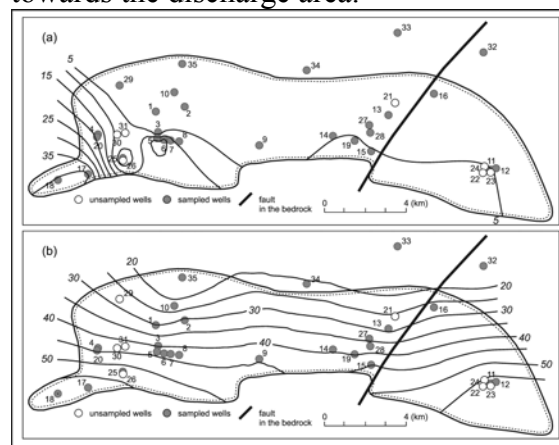


Fig. 2. Spatial distribution of ³H (a) and ¹⁴C (b) measured in 2000-2001, with isolines of ³H in TU and ¹⁴C in pmc [4].

Typical ^{14}C contents in modern waters were 35–66 pmc, whereas in wells Nos 32–34 they dropped below 0.5 pmc, with $\delta^{18}\text{O}$, $\delta^2\text{H}$ and NGT values characteristic for recharge under cooler pre-Holocene climate. Assuming that initial ^{14}C content in the system is 42 ± 12 pmc, and that the waters with lowest ^{14}C content have the age of ca. 12 ka, an effective half-life of ^{14}C in the order of 2 ka is obtained [4]. That half-life results from radioactive decay and isotope exchange of ^{14}C with carbonates present in the matrix. Although quartz is the main component of aquifer material, the carbonate content ranges from 3–10% in sands and 25–30% in sandstones. This apparent half-life of ^{14}C was confirmed by ^{40}Ar ages determined for six selected wells. Therefore, the ^{14}C and ^{39}Ar data may serve as calibration tools for the flow and transport model of the system, within the zones containing pre-modern waters.

Wide distributions of water ages, represented by RTD functions, are usually observed in abstraction wells, strongly influencing the concentration of transient tracers and pollutants, particularly in and close to recharge areas. The RTD function obtained for well No 7 represents modern water (^3H contents >10 T.U.) whereas that of well No 13 represents practically tritium-free water (Fig. 3). The later was obtained from the transport model by assuming an instantaneous appearance of a conservative tracer over the whole recharge area. Young waters are very often mixtures of water containing tracer(s) with tracer-free water in proportions easily obtainable from the RTD function. These mixing proportions are generally functions of time [2], which means that often used binary mixing models are not time-invariant.

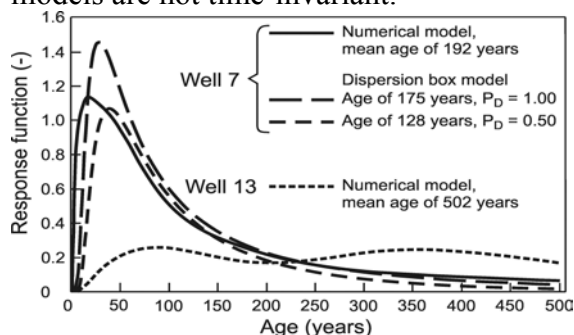


Fig. 3. Examples of RTD functions obtained from numerical and box models [3].

^{85}Kr and $^3\text{H}/^3\text{He}$ were measured in two wells in the recharge area, yielding ages of ca. 20 and 35 years, whereas tritium data yielded mean ages of ca. 60 and 160 years, respectively, for models indicating very wide RTD functions extending up to several hundred years. For the well with mean water age of 160 years, $^4\text{He}_{\text{exc}}$ of 1.7×10^{-8} $\text{cm}^3\text{STP/g}$ confirmed the presence of old component. Knowledge of RTD functions obtained either from the interpretation of tritium data, or from numerical modelling, or from both, leads to a better understanding of the aquifer response to existing or potential pollution hazards.

For some wells situated in and close to the recharge area, the simulated concentrations of transient tracers were in disagreement with the measured concentrations, even after recalibration of the numerical models, indicating the need for further improvement of the conceptual model.

Acknowledgements

J.K., K.R. and S.W. were financially supported through statutory funds of the AGH University of Science and Technology (Projects 11.11.140.139 and 11.11.220.01). P.M. was supported by grant 4T12B00428 from the Polish Committee for Scientific Research.

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Isotopically light meltwater from Scandinavian Ice Sheet in the Cambrian-Vendian aquifer system in northern Estonia: further study prospects

R. Vaikmäe¹, A. Marandi², V. Raidla^{1,2}

¹*Institute of Geology at Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; e-mail: Rein.Vaikmae@ttu.ee*

²*Institute of Geology, University of Tartu, Vanemuise 46, 51014 Tartu, Estonia*

The Cambrian-Vendian aquifer system is the lowermost of the six aquifer systems of Estonia. Its thickness amounts to 90 m and outcrops along the northern coast of Estonia on the bottom of the Gulf of Finland. The aquifer system is, as a rule, confined by 60 to 90m thick clays of the Lontova formation, having a strong isolation capacity. However, in places the bedrock formations are penetrated down to the crystalline basement by ancient buried valleys, filled mostly with loamy till but sometimes glacio-fluvial gravel occurs in the lower portion of the valleys.

Extensive isotope investigations of the groundwater were combined with geochemical studies in order to understand the processes and climate conditions during the paleorecharge, the age structure of deep waters and the mixing components and their variation. Also amount and composition of extracted gases were determined. A three-dimensional hydrodynamic model covering the whole territory of Estonia was developed for to study the groundwater dynamics.

The oxygen isotope composition of groundwater in most of aquifer systems in Estonia ranges from -11.0 to -12.2 ‰. However, the groundwater in the Cambrian-Vendian aquifer system has a heavily depleted oxygen isotope composition. The values of $\delta^{18}\text{O}$ vary mainly from -18.1 to -22‰. At the same time, the long term mean annual $\delta^{18}\text{O}$
DOI: 10.2312/GFZ.mga.046

values in contemporary precipitation in

Estonia are -10.4‰. Low $\delta^{18}\text{O}$ values in the Cambrian-Vendian aquifer are indicative of recharge in cold conditions, whilst low ^{14}C concentrations are indicative of long residence time of groundwater. In some samples unexpectedly high gas concentrations (two-five times over-saturation) have been found. Analyses of the gas composition in several cases showed rather high concentration of methane with low $\delta^{13}\text{C}$ values. This indicates that methane has most probably biogenic origin.

Based on the results of recent studies [1, 2] our current hypothesis is that Cambrian Vendian groundwater in northern Estonia formed by basal melting of Scandinavian Ice Sheet at high fluid pressure and it carries a very distinct signature of dissolved gas concentrations.

To test this concept the following new research in collaboration with Free University of Amsterdam (H. Kooi), University of Heidelberg (W. Aeschbach-Hertig) and others is planned:

- (a) Acquisition of high-quality noble gas, isotopic and hydrochemical data in Cambrian-Vendian aquifer.
- (b) Comprehensive study of ice-core data and gas-entrapment models to establish a quantitative end-member model for the gas content of basal melting recharge water.

- (c) Interpretation of existing and newly acquired data (a) in terms of basal melting signatures and mapping of occurrence and distribution of such waters.

Acknowledgments

This study has been carried out with the financial support of Estonian Science Foundation Grant no 5925 to R.V.

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Environmental Tracer Applications in aquifers with elevated As concentrations in Bangladesh

M. Stute^{1,2}, A. Horneman^{2,3}, P. Schlosser³, Y. Zheng⁴, A. van Geen³, N. Santella², W. Smethie, Jr.², D. T. Ho², K.M. Ahmed⁵, and M.A. Hoque⁵

¹*Environmental Science, Barnard College, Columbia University, 3009 Broadway, New York, NY 10027, USA,*

²*Lamont-Doherty Earth Observatory of Columbia University, 61 Rte 9W, Palisades, NY 10964, USA*

³*Department of Earth and Environmental Engineering, Columbia University, 918 Seeley Mudd Building, 500 West 120th St, New York, NY 10027, USA*

⁴*Earth and Environmental Sciences, Queens College and Graduate Center, CUNY, 65-30 Kissena Blvd, Flushing, NY 1136, USA*

⁵*Department of Geology, Dhaka University, Dhaka 1000, Bangladesh*

The elevated arsenic (As) content of groundwater from wells across Bangladesh and several other South Asian countries is estimated to slowly poison at least one hundred million people. The heterogeneous distribution of dissolved arsenic in the subsurface complicates understanding of its release from the sediment matrix into the groundwater, as well as the design of mitigation strategies.

Distributions of ³H/³He, atmospheric noble gases, ¹⁸O, ²H, CFCs, and SF₆ were determined in aquifers in Bangladesh with elevated dissolved Arsenic concentrations. Noble gas concentrations provide evidence for degassing during recharge. Stable isotopes indicate that groundwater is recharged directly by percolating precipitation and mildly evaporated surface waters. Comparison of groundwater ³H+³He data with ³H concentrations in precipitation suggests that some samples are affected by mixing with pre-bomb groundwater. CFC 11 and 12 concentrations in this reducing environment decline rapidly as a function of ³H/³He age at rates of ~0.4 to ~6 yr⁻¹ and from ~0.25 to ~5 yr⁻¹, respectively. SF₆ ages in the shallowest aquifer were generally higher than ³H/³He ages, most likely due to interactions with subsurface gas phases. SF₆ was found in ³H-free deeper

groundwater indicating the occurrence of natural SF₆ in Bangladesh aquifers. ³H/³He-derived recharge rates are consistent with hydraulic estimates. We also observed a linear correlation between ³H/³He groundwater age at depths <20 m and dissolved As concentration, with an average slope of 19 µgL⁻¹yr⁻¹ (monitoring wells only). We propose that either the kinetics of As mobilization or the removal of As by groundwater flushing is the mechanism underlying this relationship. In either case, the spatial variability of As concentrations in the top 20 m of the shallow aquifers can to a large extent be attributed to groundwater age controlled by the hydrogeological heterogeneity in the local groundwater flow system.

Excess air as indicator of recharge related nitrate pollution in groundwater of the semi-arid Kalahari, Botswana

K. Osenbrück¹, S. Stadler^{2,3}, A.O. Suckow⁴, J. Sültenfuß⁵, S.M. Weise¹

¹ Department of Isotope Hydrology, UFZ – Helmholtz-Centre for Environmental Research, Halle, Germany

² Groundwater Quality and Protection, Fed. Institute for Geosci. & Natural Resour. (BGR), Hannover, Germany

³ present address: Department of Geology, Technical University of Freiberg, Germany

⁴ Isotope Hydrology Laboratory, International Atomic Energy Agency (IAEA), Vienna, Austria

⁵ Institute of Environmental Physics and Oceanography, University of Bremen, Germany

Introduction

“Excess air” usually denotes a gas component dissolved in groundwater that is in excess to the equilibrium solubility and to other known subsurface gas sources. It was first recognised in groundwater as a by-product of infiltration temperature calculations from dissolved noble gases [1]. Since then a number of studies established the ubiquitous presence of excess air in groundwater, which has to be accounted for in the interpretation of dissolved gases (e.g. noble gases, excess nitrogen, CFCs, SF₆). Several model concepts have been proposed and successfully applied that attribute excess air to the dissolution of small air bubbles trapped in soil pores during groundwater recharge, including the total dissolution (TD), closed-system equilibration (CE), and partial re-equilibration (PR) models [2]. Yet, most studies have treated excess air as a nuisance that must be corrected for to obtain the gas component of interest. However, a few noble gas studies in semi-arid environments [3-5] reported evidence that excess-air might reflect the conditions or processes during groundwater recharge.

Study area

Here we present hydrochemical and environmental tracer investigations in groundwater from the semi-arid Kalahari in Botswana where excess air provides information on the source of nitrate pollution if used as a recharge indicator. The study

area is located on the Eastern fringe of the Kalahari close to the town of Serowe, Botswana [6]. Rainfall in the study area is restricted to one rainy season with a mean annual value of about 400 mm/yr. Groundwater samples were taken from 50 to 250 m deep wells tapping water from the fractured and mostly confined Ntane sandstone aquifer, which is affected by nitrate pollution. Because the investigated region experiences extreme water scarcity, an understanding of the origin of nitrate is of major importance for the management of the groundwater for water supply.

Results and Discussion

Nitrate concentrations in groundwater range from 2 to 210 mg/l. Stable isotopes of nitrate and water suggest that nitrate is derived from natural soil sources but not related to evaporative enrichment [6]. Combining noble gases with nitrate a strong linear correlation of nitrate with dissolved neon content is obtained for groundwater with elevated ¹⁴C DIC content (Fig. 1). Neon concentrations in groundwater are consistently found in excess when compared to solubility equilibrium, which is attributed to excess air. In Fig. 1 high nitrate concentrations correspond to neon values close to solubility equilibrium, indicating low recharge rates where neon concentrations remain close to solubility equilibrium during the slow transport of water towards the groundwater table. By contrast, low nitrate concentrations are connected to high neon excess values, suggesting that

this groundwater has been recharged at much higher rates, preventing occasionally trapped and dissolved air bubbles from complete re-equilibration. These findings

indicate that nitrate concentrations are strongly correlated with recharge dynamics prevailing at different locations or times.

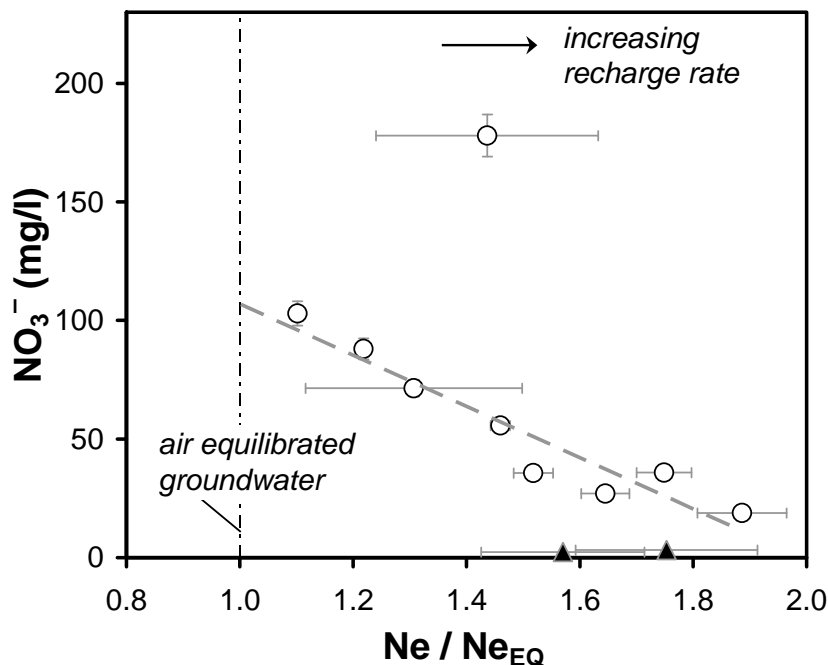


Fig. 1. Nitrate concentration versus neon concentration normalised to solubility equilibrium for the altitude (1200 m) and temperature (25°C) of recharge. Open symbols indicate ¹⁴C rich, filled symbols ¹⁴C poor samples. Error bars represent the error of measurement (2σ).

The application of excess air as proxy of recharge conditions is supported by ¹⁴C dating which indicates that low recharge rates are associated with recently recharged groundwater. This is in full agreement with estimates for the current recharge rate of less than 10 mm/yr in the semi-arid Kalahari [7,8]. Higher recharge rates several thousand years before present are in reasonable accordance with climate proxies from the Kalahari, which give evidence that several wet phases have prevailed at the end of the Pleistocene and during the Holocene [9]. During such wet climate periods intense replenishment of the aquifer apparently lead to the formation of high excess air.

Therefore, increased nitrate concentrations after transition to a drier climate are most likely related to changes in the vegetation cover, soil water balance, and recharge dynamics.

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Preliminary results of a helium / tritium monitoring of a shallow crystalline rock aquifer in Brittany : influence of pumping for drinking water supply.

E. Fourré¹, L. Aquilina², A-C. Pierson-Wickmann², P. Jean-Baptiste¹, D. Baumier¹, T. Labasque², V. Ayraud²

¹ *Laboratoire des Sciences du Climat et de l'Environnement/IPSL UMR CEA-CNRS-UVSQ Orme des Merisiers 91191 Gif sur Yvette France elise.fourre@cea.fr*

² *CAREN Géosciences UMR6118 Université Rennes1 Bat15, 263 Avenue du Général Leclerc 35042 Rennes France*

Drinking water is a key concern in Brittany, an agricultural area where intensive pig farming leads to nitrate diffuse pollution of surface and groundwaters. In the framework of a regionally funded project dedicated to a better understanding of the biogeochemical processes occurring in shallow aquifers in crystalline rocks, we take part to the helium/tritium monitoring of several sites in Brittany. One aspect of the project is to compare tritium/helium and CFC dating for young waters in such heterogeneous sites.

We present here the preliminary results of our on-going survey of the Vau Rezé site, 10km north of Rennes: besides 2 pumping equipments set up for drinking water supply, 4 piezometers were built to sample the altered schists and 3 other wells were drilled in the deeper part of the site. Although the investigated area is small (less than 0.1km²) and all the wells were drilled in the same geological formation, the geochemical results show a high spatial variability resulting of initial groundwater chemistry acquisition and mixing mechanisms [1]. Another interesting feature of this site is its pumping history: in 2001, nitrate concentration in the shallow pumped well (modified spring) exceeded the drinking water safety limit; pumping stopped and resumed only in April 2004, once the drilling of a new deep well was achieved. Our study began at that time and

we show how this anthropogenic pumping strongly affects the water He concentration and the mixing processes in some parts of the site.

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Simultaneous determination of Ne, Ar, SF₆, CFC-11 and CFC-12 in groundwater by gas chromatography

P. Mochalski, I. Sliwka, and J. Lasa

Institute of Nuclear Physics PAN Radzikowskiego 152 street, PL-31342 Krakow, Poland

Introduction

Sulphur hexafluoride (SF₆) and Freons become commonly used for dating young groundwaters whereas noble gases mainly serve for determining the temperature of recharge and the air excess which is also needed to correct measured values of SF₆ concentrations [1-3]. Usually, determination of Ne, Ar, SF₆, CFC-11 and CFC-12 requires two or three independent instrumental analyses and separate sets of samples [1, 2]. Within this work, an analytical method for simultaneous determination of all five tracers in a single sample of water is presented.

Sampling

Water samples are taken in duplicate through copper tubes into specially constructed 2.9-L stainless steel vessels. Before sampling containers are carefully flushed with high-purity nitrogen to remove air. Wells are sampled under pressure to avoid sample degassing. Contamination by air is controlled by measurements of dissolved oxygen. Samples are stored in a laboratory refrigerator at 6 °C. An effort is made to analyse them within 2 days after sampling.

Analytical method

Sample vessels are also used as measuring vessels by heads-space extraction technique (HS) [4] and gas chromatography (GC). The scheme of analytical system is shown in Fig 1.

The headspace volume is created in the sample vessel using high-purity nitrogen (99.9999%) and a syringe (S). The vessel is shaken mechanically for 20 minutes to obtain equilibrium between the gas and

liquid phase. Next, the equilibrated gas is transferred into the vacuum extraction and purification line (thickened lines in Fig 1). Dried in Nafion tube extracted HS gas fills in two sample loops (P2 and P3) and a glass 125 ml-in-volume pipette.

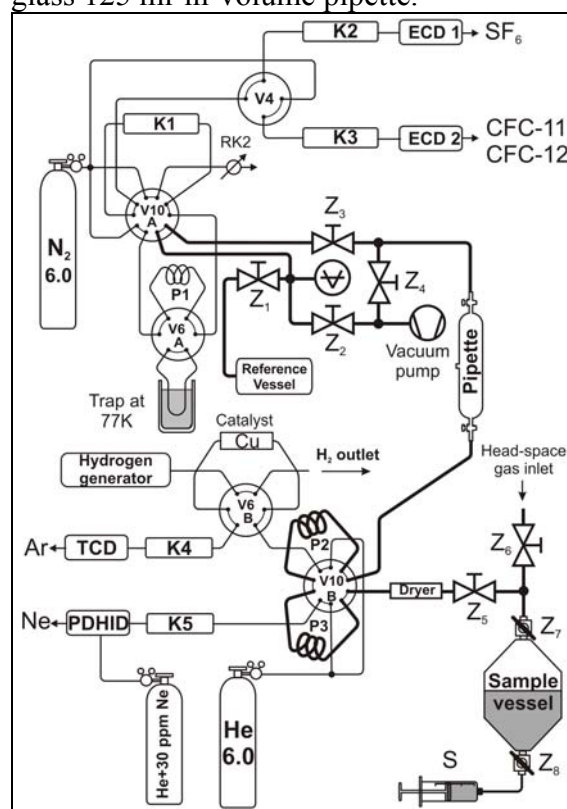


Fig 1 Scheme of measurement system.
Z₁₋₆ – Nupro valves

Neon is measured with a GC-PDHID. Carrier gas (He 6.0) transports extracted HS gas from the P3 loop (2ml) into a 30m×0.56 capillary column filled with molecular sieve 5A. Neon is detected by Valco PD-D2 detector doped with Ne (30 ppm of Ne in discharge helium) [5, 6]. Argon is analysed with a TCD detector. A 0.5 ml of gas sample (loop P2) is separated in a 1.5 m×1/8 inch packed column (K4) filled with molecular sieve 5A. Separation

of Ar and O₂ is achieved via a catalytic removal of oxygen from the sample at elevated temperature (grains of Cu at 200°C) [6]. The catalyst is periodically activated using hydrogen.

SF₆ and CFCs are measured using three chromatographic columns operating in a back-flush mode, and two electron capture detectors (ECD) [7]. The extracted HS gas filling the glass pipette (125 ml) is cryofocused (77 K) under lowered pressure on a trap packed with glass pellets. After desorption gases are injected into a 2 m×1/8" column (K1) filled with n-octan on Porasil C. This column is connected for particular time intervals to a 3 m×1/4" column (K2) packed with 5Å molecular sieve and next to a 0.5 m×1/8" column (K3) filled with n-octan on Porasil C. Column K1 works in a back-flush mode. SF₆ is detected in the ECD1 detector, whereas CFCs in the ECD2. The measurements are calibrated against standards obtained from Linde gas (Ne and Ar) and from the Scripps Institution of Oceanography, San Diego, USA (SF₆ and CFCs).

Typical chromatograms of a water sample are presented in Fig. 2.

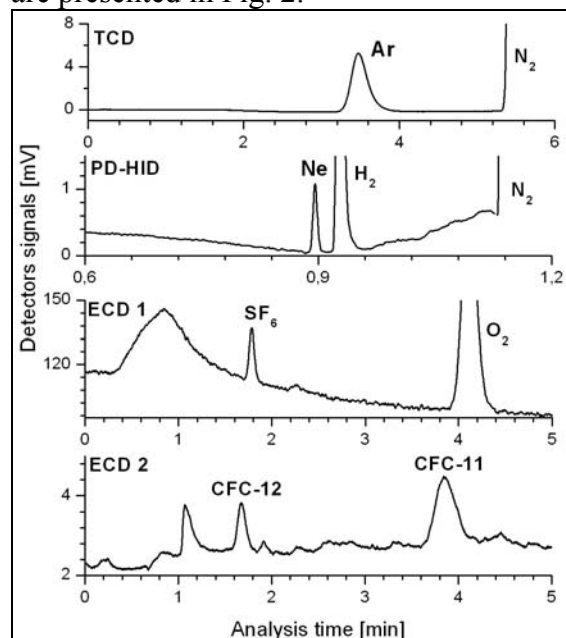


Fig 2 An example of chromatograms from groundwater analysis

The total analysis time is 50 minutes, including extraction and cryofocusing. Detection limits for measured tracers are 0.06

fmol/L (0.0081 pg/kg) for SF₆, 15 fmol/L (2.1 pg/kg) for CFC-11, 10 fmol/L (1.23 pg/kg) for CFC-12, 0.84 nmol/L (1.9×10^{-8} cm³_{STP}/cm³) for Ne and 0.15 μmol/L (3.1×10^{-6} cm³_{STP}/cm³) for Ar. The reproducibility estimated for modern water sample is 1.6% for Ne, 0.8% for Ar and 5% for SF₆ and CFCs.

Conclusions

Simultaneous measurement of Ne, Ar, SF₆, CFC-11 and CFC-12 in groundwater has numerous advantages. The number of samples needed to obtain all tracers data as well as sampling time is significantly reduced. Relatively inexpensive gas chromatographic technique reduces analysis cost and laboratory effort.

Acknowledgments

This work was financially supported by the Polish Committee for Scientific Research (grants 4T12B.004.28 and 3.T09D.038.29 in the time period of 2006-2008).

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List of Participants

Prof. Werner Aeschbach-Hertig
Institute for Environmental Physics
Heidelberg University
INF229
69120 Heidelberg
GERMANY
aeschbach@iup.uni-heidelberg.de

Robert Annewandter
Carl Friedrich von Weizsäcker-Zentrum
für
Naturwissenschaft und Friedensforschung
der Universität Hamburg
Martin-Luther-King-Platz 6
20146 Hamburg
GERMANY
robert.annewandter@physnet.uni-hamburg.de

Dr. Anne Battani
IFP
1 & 4 avenue de Bois preau
92500 Rueil Malmaison
FRANCE
anne.battani@ifp.fr

Catherine Beland-Otis
Université du Québec
Départ. Sci. de la Terre et de l'Atmosphère
and GEOTOP-UQAM-McGill à Montréal
Succ. Centre-Ville
CP 8888, Montréal, Québec; H3C 3P8
CANADA
Catherine.beland.otis@gmail.com

Prof. Clara-Maria Castro
University of Michigan
Department of Geological Sciences
2534 C. C. Little Building, Ann Arbor
MI 48109-1063
USA
mccastro@umich.edu

Prof. Jordan F. Clark
Earth Science
University of California
Santa Barbara, CA 93106-9630
USA
jfclark@geol.ucsb.edu

Dipl. Phys. Heiner Daerr
Carl Friedrich von Weizsäcker-Zentrum
für
Naturwissenschaft und Friedensforschung
der Universität Hamburg
Martin-Luther-King-Platz 6
20146 Hamburg
GERMANY
Heiner.daerr@uni-hamburg.de

Prof. Jörg Erzinger
Inorganic & Isotope Geochemistry, Head
GeoForschungsZentrum Potsdam
Telegrafenberg B324
14473 Potsdam
GERMANY
erz@gfz-potsdam.de

Elise Fourre
Lab. Sci. du Climat et de l'Environnement
IPSL UMR
CEA-CNRS-UVSQ Orme des Merisiers
91191 Gif sur Yvette
FRANCE
Elise.Fourre@cea.fr

Dipl. Phys. Ronny Friedrich
Institute for Environmental Physics
Heidelberg University
INF229
69120 Heidelberg
GERMANY
ronny.friedrich@iup.uni-heidelberg.de

Dr. Manfred Gröning
Isotope Hydrology Laboratory, Head
International Atomic Energy Agency
Wagramerstr.5
1400 Vienna
AUSTRIA
m.groening@iaea.org

Prof. Nilgun Gulec
Middle East Technical University
Department of Geological Engineering
06531, Ankara
TURKEY
nilgun@metu.edu.tr

List of Participants

Prof. David Hilton
University of California at San Diego
Geosciences Research Division
0244 Scripps Instit. of Oceanography
La Jolla, California
USA 92093.
drhilton@ucsd.edu

Dr. Chris Hall
University of Michigan
Dept of Geological Sciences
2534 CC Little Bldg
1100 North University Ave
Ann Arbor, MI 48109-1005
USA
cmhall@umich.edu

Markus Hofer
Eawag
Swiss Federal Institute of
Aquatic Science and Technology
CH 8600 Dübendorf
SWITZERLAND
Markus.hofer@eawag.ch

Dr..Andrew G. Hunt
U.S. Geological Survey
Noble Gas Laboratory
Denver, Colorado
USA
ahunt@usgs.gov

Prof. Philippe Jean-Baptiste
LSCE
CEA-Saclay
91191 - Gif/Yvette
FRANCE
Philippe.Jean-Baptiste@cea.fr

Dipl. Phys. Tobias Kluge
University of Heidelberg
Institute of Environmental Physics
69120 Heidelberg
GERMANY
Tobias.kluge@iup.uni-heidelberg.de

Dipl. Phys. Markus Kohler
Carl Friedrich von Weizsäcker-Zentrum für
Naturwissenschaft und Friedensforschung
der Universität Hamburg
Martin-Luther-King-Platz 6
20146 Hamburg
GERMANY
Markus.kohler@uni-hamburg.de

Prof. Henk Kooi
Department of Hydrology and
Hydrogeology
Faculty of Earth & Life Sciences
Vrije Universiteit
De Boelelaan 1085
1081 HV Amsterdam
THE NETHERLANDS
Henk.kooi@falw.vu.nl

Dipl. Phys. Andreas Kreuzer
Heidelberg University
Institute for Environmental Physics
69120 Heidelberg
GERMANY
Andreas.kreuzer@iup.uni-heidelberg.de

Dr. Bernard Lavielle
University Bordeaux 1-2
Chimie Nucléaire Analytique e
Bioenvironnementale
CNAB
UMR 5084 CNRS
Le Haut Vigneau, BP120
33175 Gradignan Cedex
FRANCE
lavielle@cenbg.in2p3.fr

Dr. Johanna Lippmann-Pipke
GeoForschungsZentrum Potsdam
Telegrafenberg B323
14473 Potsdam
GERMANY
lippmann@gfz-potsdam.de

List of Participants

Dr. Andrew Manning
U.S. Geological Survey
P.O. Box 25046, Mail Stop 964
Denver, CO 80225 USA
USA
amanning@usgs.gov

Prof. Bernard Marty
CRPG
BP20
54501 Vandoeuvre les Nancy Cedex
FRANCE
bmarty@crpg.cnrs-nancy.fr

Prof. Michael McWilliams
John de Laeter Centre of Mass
Spectrometry
Curtin University
GPO Box U1987
Perth, WA
AUSTRALIA

Dr. Pawel Mochalski
Instytut Fizyki Jądrowej im.
Henryka Niewodniczańskiego PAN
31-342 Kraków, ul.
E. Radzikowskiego 152
POLAND
Pawel.Mochalski@ifj.edu.pl

Dr. Jean E. Moran
Lawrence Livermore National Lab
L-231, P.O. Box 808
Livermore, CA 94551
USA
moran10@llnl.gov

Dr. Halim Mutlu
Depart. of Geological Engineering
Eskişehir Osmangazi University
26480, Eskişehir
TURKEY
hmutlu@ogu.edu.tr

Prof. Keisuke Nagao
University of Tokyo
Laboratory for Earthquake Chemistry
Graduate School of Science
Tokyo 113-0033
JAPAN
nagao@eqchem.s.u-tokyo.ac.jp

Dr. Samuel Niedermann
GeoForschungsZentrum Potsdam
Telegrafenberg B321
14473 Potsdam
GERMANY
nied@gfz-potsdam.de

Dr. Karsten Osenbrück
UmweltForschungsZentrum UFZ
Theodor-Lieser-Straße 4
06120 Halle (Saale)
GERMANY
karsten.osenbrueck@ufz.de

Dr. Laslo Palcsu
University Heidelberg
Institute of Environmental Physics
Im Neuenheimer Feld 229
69120 Heidelberg
GERMANY
Laslo.Palcsu@iup.uni-heidelberg.de

Prof. Daniele Pinti
Université du Québec à Montréal
Départ. Sci. de la Terre et de l'Atmosphère
CP 8888
Succ. Centre-Ville
Montréal, Québec; H3C 3P8
CANADA
Pinti.daniele@uqam.ca

Dr. Roland Purtschert
Universität Bern
Physikalisches Institut
Klima- und Umwelphysik
Sidlerstr. 5
3012 Bern
SWITZERLAND
purtschert@climate.unibe.ch

List of Participants

M.Sc.Eng. Joanna Pusz
The Henryk Niedwodniczański
Institute of Nuclear Physics
Radzikowskiego Str. 152
31342 Kraków
POLAND
jpusz@poczta.fm

Prof. Kazimierz Rozanski
AGH University of Technology Krakow
Mickiewicza 30
30059 Kraków
POLAND
rozanski@novell.ftj.agh.edu.pl

Prof. Yuji Sano
The University of Tokyo
Center for Advanced Marine Research
Ocean Research Institute
Minamidai 1-15-1,
Nakano-ku, Tokyo 164-8639
JAPAN
ysano@ori.u-tokyo.ac.jp

Prof. Peter Schlosser
Columbia University
Lamont-Doherty Earth Observatory
61 Route 9W, PO Box 1000
Palisades, New York 10964
USA
schlosser@ldeo.columbia.edu

Prof. Ireneusz Sliwka
Depart. of Physicochemistry of
Ecosystems
The Henryk Niewodniczanski Institute
of Nuclear Physics
Polish Academy of Sciences,
Radzikowskiego Str. 152
31342 Krakow
POLAND
Ireneusz.Sliwka@ifj.edu.pl

Dr. Nicole Stroncik
GeoForschungsZentrum Potsdam
Telegrafenberg B123
14473 Potsdam
GERMANY
nicole@gfz-potsdam.de

Prof. Neil C. Sturchio
Depart. Earth and Environmental Sciences
University of Illinois at Chicago
845 West Taylor Street, MC-186
Chicago, IL 60607-7059
USA
sturchio@uic.edu

Prof. Martin Stute
Lamont-Doherty Earth Observatory
& Barnard College
61 rte 9W
Palisades, NY 10964
USA
martins@ldeo.columbia.edu

Dr. Axel Suckow
International Atomic Energy Agency
Wagramer Strasse 5
1400 Wien
AUSTRIA
a.suckow@iaea.org

M. Sc. Geol. Eng. Selin Suer
Middle East Technical University
Depart. of Geological Engineering
06531, Ankara
TURKEY
ssuer@metu.edu.tr

Dr. Jürgen Sültenfuß
Institut für Umweltphysik
Universität Bremen
Abteilung Ozeanographie
Postfach 330 440
28334 Bremen
GERMANY
suelten@uni-bremen.de

Prof. Dario Tedesco
University of Naples 2
Geochemistry & Volcanology, Chair
Depart. of Environmental Sciences
Via Vivaldi 43
81100 Caserta
ITALY
dtedesco@unina.it

List of Participants

Dr. Bertrand Thomas
University Bordeaux 1-2
CNAB, CNRS UMR 5084
CNAB
UMR 5084 CNRS
Rue du Solarium, BP120
33175 Gradignan Cedex,
FRANCE
thomasb@cenbg.in2p3.fr

Yama Tomonaga
Eawag
Swiss Federal Institute of
Aquatic Science and Technology
Überlandstrasse 133
Postfach 611
8600 Dübendorf
SWITZERLAND
tomonaga@eawag.ch

Prof. Rein Vaikmäe
Institute of Geology at
Tallinn University of Technology
Ehitajate tee 5
19086 Tallinn
ESTONIA
rein.vaikmae@ttu.ee

Prof. Stephen J. Van der Hoven
Department of Geography-Geology
Illinois State University
Campus Box 4400
Normal, IL 67190-4400
USA
vanderhoven@ilstu.edu

Dr. Stephan Weise
Helmholtz Centre for Environmental Res.
UFZ
Department of Isotope Hydrology
Theodor-Lieser-Straße 4
06120 Halle (Saale)
GERMANY
stephan.weise@ufz.de

Dr. Thomas Wiersberg
GeoForschungsZentrum
Telegrafenberg
14473 Potsdam
GERMANY
wiers@gfz-potsdam.de

Dipl. Phys. Martin Wieser
Institute for Environmental Physics
Heidelberg University
INF229
69120 Heidelberg
GERMANY
martin.wieser@iup.uni-heidelberg.de

Dr. Gisela Winckler
Columbia University
Lamont-Doherty Earth Observatory
61 Route 9W, Palisades, NY 10964
USA
winckler@ldeo.columbia.edu

Dr. Reika Yokochi
University of Illinois at Chicago
Depart. Earth and Environmental Sciences
845 W. Taylor Street, Chicago
IL 60607-7059
USA
yokochi@uic.edu

Dr. Zheng Zhou
The University of Manchester
School of Earth
Atmospheric and Environm. Sciences
UK
Zhou.eth@gmail.com

Prof. Dr. Andrzej Zuber, retired from the
Institute of Nuclear Research, Krakow
occasionally employed by the
Polish Geological Institute
Carpathian Branch
ul. Skrzatow 1
31560 Krakow
POLAND
zuber@novell.ftj.agh.edu.pl

or A. Zuber, Friedleina 13/4
30009 Krakow, POLAND

