

Concentrations and behaviors of I and Br in soil-plant systems

S. UCHIDA¹* AND K. TAGAMI

¹Natl. Inst. Radiol. Sci., 4-9-1 Anagawa, Chiba 263-8555, Japan (*correspondence: s_uchida@nirs.go.jp)

Iodine Behaviour in Terrestrial Environment

It is well known that dry and wet deposition from the marine environment is an important source of I and Br into the terrestrial environment. Methylation of these elements, which are ozone-depleting substances, can occur in certain terrestrial plants, so that their behavior in the terrestrial environment is of special interest in soil-plant systems. We developed a simple method to measure I and Br in soil and plant samples by ICP-MS. Tetramethyl ammonium hydroxide was used to extract I and Br from these samples under relatively mild condition (60°C).

Concentrations of I and Br and Crop Uptake

The method can successively recover ca. 100% of I and Br from soil and plant samples. Using the method, we measured 92 paired samples of crop and soil. The relation between I and Br concentrations in the upland field and paddy field soil samples is shown in Figure 1. Concentrations of I and Br were highly correlated in both upland fields and paddy fields showing $r=0.86$ ($p<0.001$) and $r=0.84$ ($p<0.001$), respectively. However, I and Br concentrations were low in paddy field soils, possibly because the fields were covered with water during rice planting period which can cause low redox conditions. Plant uptake behavior of I and Br will be discussed.

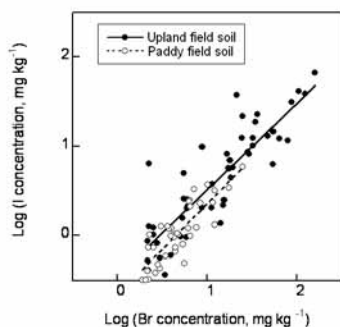


Figure 1: Correlation between I and Br concentrations in agricultural soils.

This work has been partially supported by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade and Industry (METI), Japan.

Nanogold and its bearing on “invisible Gold” in sulfides

S.S. UDUBASA¹*, L. PETRESCU¹, S. CONSTANTINESCU², N. POPESCU-POGRION² AND G. UDUBASA¹

¹University of Bucharest, Bucharest 010041, Romania (*correspondence: udubasa@geo.edu.ro)

²National Institute of Materials Physics, Bucharest-Magurele 077125, Romania (sconst@infim.ro)

Natural gold shows a great variety of forms and size, mainly due to its high chemical stability and mechanical coherence. In addition to macro- and microgold it was shown that nanogold might also exist, as a supplementary alternative to the “invisible gold”, supposedly substituting for As and Fe, e.g. in arsenopyrite (see [1] and many others thereafter). Nanogold forms both spherical, isolated grains and coral-like aggregates, several nanometers and tens of nanometers in size, respectively [2]. It was first detected on grain surfaces of nearly all the sulfides present in some small-size shear-zone related gold ores in metamorphics, however with a preference for arsenopyrite and pyrite.

The nanogold was identified by using a combination of physical methods, i.e. TEM/SAED, HRTEM and NGR (Mössbauer), following careful electron microscopic investigation on selected samples. The distribution of nanogold seems to be aleatory, following its apparently random distribution in all the ore types. However, the selectivity of nanogold seems to be related to crystalchemical features of host sulfides: arsenopyrite with different Fe/As ratios, As-bearing varieties of pyrite, pyrrhotite (a typical non-stoichiometric compound) and chalcopyrite (proved by NRG to contain both bivalent and trivalent iron). Such features obviously allow n and p junctions at the grain boundaries to appear, i.e. ideal loci for nanogold (seemingly with residual electrical charges like nearly all the nanomaterials) to concentrate.

Nanogold is seemingly refractory to majority of technological recovery processes. In an ongoing project undertaken at the University of Bucharest concerning phytorecovery of gold from geological materials with low to very low gold contents, is currently investigated the availability of gold to plants concentration, supposedly at a maximum for nanogold.

[1] Cathelineau *et al.* (1989) *Econ. Geol. Monograph* **6**, 328-341, [2] Udubasa *et al.* (1996) *Progr. & Abstr. 6th Seeheim Workshop on Mössbauer Spectroscopy*, 2006 Seeheim, Germany, Section **C-19**.

Geochemical results on the CO₂ georeactor sequestration tests at the Ogachi hot dry rock site, NE Japan

A. UEDA^{1*}, Y. NAKATSUKA¹, M. KUNIEDA¹,
Y. KURODA¹, K. KATO^{2,4}, T. YAJIMA², H. SATOH²,
Y. ODASHIMA², K. SUGIYAMA³, A. OZAWA³,
T. OHSUMI⁴, H. WAKAHAMA⁴, S. MITO⁴, Y. KAJI⁵ AND
H. KAIEDA⁶

¹Kyoto Univ., C1-2-155, Katsura, Kyoto, 615-8540, Japan
(*correspondence: a-ueda@earth.kumst.kyoto-u.ac.jp)

²Mitsubishi materials Corp., Kitabukuro, Omiya, Saitama,
Japan (koikato@mmc.co.jp, tyajima@mmc.co.jp,
hsatoh@mmc.co.jp, yodasima@yahoo.co.jp)

³Mitsubishi Materials Natural Resources development Corp.,
Kitabukuro, Omiya, Saitama, Japan (sgym@mmc.co.jp,
aозawa@mmc.co.jp)

⁴Research Institute of Innovative Technology for the Earth,
Kizugawadai, Kizu, Kyoto, Japan (ohsumi@rite.or.jp,
wakahama@rite.or.jp; mito@rite.or.jp)

⁵Chuo Kaihatsu Corp., Kawaguchi, Saitama, 332-0035, Japan
(kaji@cknet.co.jp)

⁶Central Research Institute of the Electric Power Industry,
Abiko, Chiba, Japan (kaieda@criepi.denken.or.jp)

Field Experiments

Field experiments of CO₂ sequestration into the Ogachi HDR have been examined for 4 years by our group. There are two injection/production wells (OGC-1 and 2), two major feed zones at depth of 700m and 1100m, where their temperatures are 170 and 210°C, respectively. CO₂ dissolved water (river water with dry ice) was directly injected into OGC-2 with tracers. Water samples are collected at the depth of ca. 800m by a sampler and monitored for their chemical and isotopic compositions. Dissolution or precipitation rates of calcite were determined by using a new technique of “*in situ* analyses” at the depth.

Results

The CO₂ and tracer concentrations decrease with the elapsed time. The injected CO₂ water is diluted with the reservoir fluid with 3 days and most CO₂ in them might be deposited as calcite by interaction with granitic rocks. The “*in situ* analyses” show that calcite precipitation was observed within 2 day after the injection. This supports the view that most of CO₂ injected might be fixed as carbonate.

Biological fractionations of quadruple sulfur isotopes in a stratified lake

Y. UENO¹, M. NAKAGAWA² AND N. YOSHIDA³

¹Global Edge Institute, Tokyo Institute of Technology,
Meguro, Tokyo, 152-8551, Japan
(ueno.y.ac@m.titech.ac.jp)

²Department of Applied Chemistry, Tokyo Institute of
Technology, Meguro, Tokyo, 152-8551, Japan

³Department of Environmental Science and Technology,
Tokyo Institute of Technology, Midoriku, Yokohama,
226-8603, Japan

Quadruple sulfur isotope system (³²S/³³S/³⁴S/³⁶S) is a potential new tracer not only for photochemically-induced non-mass-dependent reactions, but also for mass-dependent processes including biogeochemical reactions [1]. We have studied quadruple sulfur isotope ratios of sulfate and sulfide in a small monomictic lake Fukami-ike, central Japan, having a maximum depth of 8.0 m. The lake is eutrophic and is stratified from March to October, when green and purple sulfur bacteria (anaerobic photosynthesizer) are active at oxic-anoxic boundary layer, and sulfate reducing bacteria produces hydrogen sulfide accumulated in an anoxic hypolimnion [2]. In August, systematic changes of δ³⁴S as well as Δ³³S and Δ³⁶S values was observed both for sulfate and sulfide in anoxic hypolimnion. Simple calculation assuming Rayleigh process yielded fractionation factors for ³⁴S/³²S (α-34) of 0.980, and mass dependent exponents λ-33 and -36 of 0.505 and 1.93, respectively. The results are consistent with sulfate reduction within a water column of the lake. Moreover, seasonal variation of Δ³⁶S/Δ³³S relationship demonstrated that ³³S and ³⁶S signatures are potential indicators not only for microbial sulfate reduction but also for different sulfur metabolisms or cycles.

[1] Johnston *et al.* (2007) *GCA* **71**, 3929-3947. [2] Yagi (1996) *Water Resources Research* **30**, 1823-1832.

Differentiation of mantle-derived calc-alkaline magmas at mid to lower crustal levels: Experimental and petrologic constraints

P. ULMER^{1*}, O. MÜNTENER² AND R. ALONSO PEREZ¹

¹Department of Earth Sciences, ETH-Zurich, CH-8092 Zurich, Switzerland (peter.ulmer@erdw.ethz.ch)

²Institute of Mineralogy and Geochemistry, University of Lausanne, CH-1015 Lausanne, Switzerland

This contribution compares experimentally derived liquid-lines-of-descent on primary, hydrous calc-alkaline magmas ranging from picrobasaltic to basaltic andesite at pressures of 1bar to 15 kbar with geochemical evolutionary trends of contrasting subduction related continental arc systems, namely the Adamello batholith, the Kohistan Arc and the Cascadian Arc system.

Field, petrologic and geochemical data of all three systems are indicative for polybaric crystallization over basically the entire crustal column. This is clearly supported by experimental data that reveal that the majority of basic to intermediate rock compositions are not only close to the liquid line of descent indicating that crystal retention in plutonic systems is not very efficient in basaltic to intermediate magmas, but also that the mean crystallization pressures obtained from oxide-oxide variation diagrams are in the range 5-15 kbar consistent with deep-level (crust-mantle boundary) and intermediate crustal level (15-25 km) magma storage areas where the principal crystallization-driven differentiation took place. In the case of the southern Adamello, subtle differences in the liquid-lines-of-descent are fully consistent with experimental data and trace element geochemistry indicating that different rock suites (plutons) have acquired their major and trace element characteristics at different crustal levels. The principal difference in crystallization-differentiation with increasing depth is the decreasing plagioclase stability leading to delay of the onset of plagioclase crystallization and the enhancement of earlier clinopyroxene, amphibole, and, in the case of the Kohistan arc, garnet, crystallization with increasing depth shifting derivative liquids closer to the metaluminous / peraluminous limit or even within the peraluminous field with increasing pressure, fully consistent with the geochemical evolution of associated granitoid plutonics that partly evolve to peraluminous compositions that cannot be linked to extensive crustal assimilation.

Nano-scale structure and stability of biogenic Uranium(IV) oxide

K.-U. ULRICH¹, E.J. SCHOFIELD², J.R. BARGAR², J.O. SHARP³, H. VEERAMANI³, R. BERNIER-LATMANI³, A. SINGH¹ AND D.E. GIAMMAR¹

¹Dept. of Energy, Environmental & Chemical Engineering, Washington University, St. Louis, MO 63130, USA (k.ulrich@seas.wustl.edu, giammar@wustl.edu)

²Stanford Synchrotron Radiation Laboratory, Menlo Park, CA 94025, USA (bargar@slac.stanford.edu)

³Environmental Microbiology Laboratory, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

The chemical stability of biogenic U(IV) oxide, a product of environmental bioremediation, is a seminal issue for successful U immobilization. Fundamental differences in particle size and crystal structure with synthetic UO_{2+x} ($x \sim 0$), such as disorder and hyperstoichiometry ($0 < x < 0.25$), are expected to substantially impact the stability of biogenic UO_2 in groundwater.

Biogenic UO_2 nanoparticles (~3.5 nm diameter) formed by *Shewanella oneidensis* MR-1 both at pH 6.3 and 8.0, were compared to their abiotic analog with respect to local and long-range atomic and nano-scale structures as well as dissolution kinetics under environmentally relevant conditions. Synchrotron-based powder diffraction, X-ray absorption spectroscopy, and transmission electron microscopy provided structural insight. Dissolution rates were quantified by continuous flow-through experiments under anoxic or oxidizing conditions.

The biogenic and synthetic UO_2 exhibited similar equilibrium solubility and the lowest dissolution rates under reducing, near neutral pH conditions. The rates increased logarithmically with decreasing pH. Similar surface area-normalized rates for the two solids suggest similar reactive surface site densities. This finding is consistent with the discovered structural homology of the two solids with the interior of the particles being consistent with an uncompressed fcc lattice, whereas a ~1 nm thick outer zone exhibits local static disorder similar to that in UO_{2+x} .

The presence of carbonate increased the dissolution rate of biogenic UO_2 almost to the value obtained under oxidizing conditions, and as much greater than that of synthetic UO_2 . Thus, biogenic UO_2 particles are more susceptible to surface oxidation by water and reactive oxidants originating from α -radiolysis of adjacent water. Even in anoxic aquifers, UO_2 dissolution may be controlled by thermodynamics of surface U(VI) rather than U(IV) phases.

Origin of high μ isotope signature in late Archean granitoids

T. ULRICH¹, B.S. KAMBER¹, R. MOHAN MEKALA¹ AND M.J. WHITEHOUSE²

¹Department of Earth Sciences, Laurentian University, Sudbury, Canada (tulrich@laurentian.ca)

²Laboratory for Isotope Geology Swedish Museum of Natural History, Stockholm, Sweden

The 2.8Ga Long Lake igneous suite of the Beartooth Mountains, Wyoming Craton, is characterized by elevated (high μ) $^{207}\text{Pb}/^{206}\text{Pb}$ but relatively mantle-like Sr and Nd isotope compositions. Mueller and Wooden [1] proposed that this phenomenon and the homogeneity in initial Pb isotopes is most easily explained by addition of sedimentary crustal Pb to a mantle source, hence implying the operation of sediment recycling as far back as 2.8Ga. The alternative explanation is that the high μ Pb was inherited from crustal contamination.

Here we present new Pb isotope data that confirm the high μ character of this suite but also demonstrate a previously unrecognized isotopic heterogeneity, particularly in the leached feldspar data. We also present >2,000 in situ LA-ICP-MS zircon U/Pb dates that show a clear element of zircon inheritance from crustal sources ranging in age between 2.9 and 3.5Ga. This we take as prima facie evidence for crustal assimilation. New whole rock trace element data, including many fluid-sensitive elements (B, Tl, W, As, Pb, Sb) show that most of the Long Lake gneisses are true adakites, interpreted as direct melts of eclogite facies subducted oceanic crust. These melts are inherently depleted in fluid mobile elements, including Pb but relatively enriched in Sr and Nd. Therefore, relatively mild crustal contamination is most readily seen in Pb isotopes while Nd and Sr are progressively more resilient to the crustal input.

[1] Mueller & Wooden (1988) *Geology* **16**, 871-874.

Geophysical imaging of the fluid distribution in active orogens

M.J. UNSWORTH

Institute for Geophysical Research, University of Alberta, Edmonton, AB, T6G 0B9, Canada

Geological studies of ancient orogens have shown that fluids play an important role in the evolution of these regions. Geophysical data can complement geological studies by providing constraints on the present day fluid distribution. Seismic exploration can be used to delineate these fluids. However, the presence of fluids has a much greater effect on electrical resistivity than the seismic velocity. Remote sensing of subsurface resistivity can be achieved with the magnetotelluric (MT) method which uses natural radio signals to image to depths in excess of 200 km. In this presentation I will describe how recent MT studies of active orogens can be used to determine the amount, and type of fluids in the crust and upper mantle.

An extensive set of magnetotelluric data was collected as part of the INDEPTH investigation of the India-Asia collision zone in Tibet. Models derived from these data reveal a pervasive zone of mid-crustal low resistivity that extends across the north-south extent of the Tibetan Plateau. The resistivity values can be explained with an elevated fluid content; either partial melt and/or aqueous fluids. Unsworth *et al.* [1] showed that the fluid fraction in Southern Tibet is high enough to weaken the crust and is consistent with zones of crustal flow. Similar features have been observed in the crust beneath the Arabia-Eurasia collision in Eastern Anatolia.

Subduction zones have also been studied with magnetotelluric data. Soyer and Unsworth [2] showed that in the Cascadia subduction zone, fluid pathways could be mapped above the subducting slab. In the back arc region the magnetotelluric data reveal a shallow asthenosphere. The elevated conductivities in this region can be explained by either dry partial melting, or a lower fraction of water saturated melt.

Most previous geophysical studies of orogenic belts have collected data on a series of linear profiles. However, new studies such as USArray are proceeding with fully 3D magnetotelluric imaging and are systematically imaging entire orogens, not just selected transects. This approach will result in more reliable images of subsurface fluid distribution.

[1] Unsworth *et al.* (2005) *Nature* **438**, 78-81. [2] Soyer & Unsworth (2006) *Geology* **34**, 53-56.

Lithium in Jack Hills Zircon: Evidence for extreme weathering of Earth's crust at 4300 Ma

T. USHIKUBO^{1*}, N.T. KITA¹, A.J. CAVOSIE²,
S.A. WILDE³, R.L. RUDNICK⁴ AND J.W. VALLEY¹

¹University of Wisconsin-Madison, Madison, WI 53706 USA
(*correspondence: ushi@geology.wisc.edu)

²University of Puerto Rico, Mayagüez, Puerto Rico, 00681
USA

³Curtin University of Technology, Perth, WA 6102 Australia

⁴University of Maryland, College Park, MD 20742 USA

In situ Li analyses of early Archean detrital zircons from Jack Hills, Western Australia (4.3 to 3.4 Ga) by SIMS reveal that the Li abundances (typically 10 to 60 ppm) are over 1000 times higher than in zircons crystallized from mantle-derived magmas and in mantle-derived zircon megacrysts (typically <8 ppb). The Jack Hills zircons also have fractionated lithium isotope ratios ($\delta^7\text{Li} = -19$ to $+13$ ‰), which are about five times more variable than those recorded in oceanic basalts (2-8 ‰) (e.g. [1]).

Multiple spot analyses and Li ion imaging of zircons from the Jack Hills and from granulite facies migmatites in the Adirondack Mountains reveal that Li concentration and $\delta^7\text{Li}$ correlate with CL zoning. Correlation of Li with REE, Y, and P suggests that Li substitutes via an interstitial mechanism and that Li^{+1} is important to charge balance REE^{+3} in the zircon structure. These results indicate that zircon preserves primary igneous Li compositions even if it has been subjected to prolonged high-grade metamorphism. Thus, Li composition can be used to characterize the origin of the host magma from which the zircons crystallized.

The high Li concentration, coupled with the extremely low $\delta^7\text{Li}$ observed in zircons as old as ~4300 Ma, suggests evolution in a magma contaminated by highly weathered crustal material (such as saprolite or laterite) [2, 3]. Thus, Li compositions of Jack Hills zircons strongly support the existence of chemically differentiated crust, sub-aerial weathering, and oceans as early as 4300 Ma.

[1] Tomascak (2004) *Rev. in Mineral. Geochem.* **55**, 153-195.

[2] Kisakürek *et al.* (2004) *Chem. Geol.* **212**, 27-44.

[3] Rudnick *et al.* (2004) *Chem. Geol.* **212**, 45-57.

Coffinite and ningyoite from the natural nuclear reactor at Bangombé, Gabon

S. UTSUNOMIYA¹, A.P. DEDITIUS², V. POINTEAU^{2,3} AND
R.C. EWING²

¹Department of Chemistry, Kyushu University, Fukuoka-Shi,
810-8560, Japan

²Department of Geological Sciences, University of Michigan,
Ann Arbor, MI 48109-1005, USA

³CEA Saclay, DPC/SECR, F-91191 Gif-sur-Yvette Cedex,
France

P-rich coffinite, $\text{U}(\text{Si,P})\text{O}_4 \cdot \text{H}_2\text{O}$, from the natural nuclear reactors in Bangombé, Gabon, is an important phase that incorporates percent levels of actinides and fission products. We have examined sample BAX03 (depth 12.2-12.3m) from Bangombé in order to understand micro- and nano-scale crystallo-chemical properties of P-coffinite.

Electron microprobe analysis (EMPA) was completed only on coffinite inclusions (~100 μm in size) in quartz to minimize the effect of alteration to U(VI)-phosphates and -sulfates. Based on the Si/P ratios three different chemical compositions; i) coffinite (<1.45 wt.% of P_2O_5) without uraninite inclusions, ii) P-coffinite, and iii) Si-ningyoite, $(\text{U,Ca,Ce})_2(\text{PO}_4)_2 \cdot 1-2\text{H}_2\text{O}$. Phases ii) and iii) have inclusions of uraninite. The composition of coffinite i) is expressed to be $(\text{U}_{0.79}\text{Ca}_{0.05}\text{REE}+\text{Y}_{0.04})_{0.88}(\text{Si}_{1.03}\text{P}_{0.05})_{1.08}\text{O}_4$. The amount of $(\text{Y}+\text{REE})_2\text{O}_3$ is <1.9 wt.%. Phosphorous substitutes for Si as evidenced by its negative correlation with Si ($R^2=0.87$) and positive correlation with Y+REE ($R^2=0.6$). The formula of P-coffinite (ii) is $(\text{U}_{0.71-0.88}\text{Ca}_{0.06-0.11}\text{REE}+\text{Y}_{0.07-0.18})_{0.92-1.08}(\text{Si}_{0.39-0.59}\text{P}_{0.28-0.4}\text{S}_{0.03-0.12})_{0.8-0.96}\text{O}_4$, and the P_2O_5 and $(\text{REE}+\text{Y})_2\text{O}_3$ are as high as 9.3 wt.% and 8.64 wt.%, respectively. There is a positive correlation between Ca and P ($R^2=0.62$), but no correlation among P, Y+REE and Si. The chemical formula of Si-rich ningyoite is $(\text{U}_{1.43-1.73}\text{REE}+\text{Y}_{0.2-0.3}\text{Ca}_{0.18-0.23})_{1.88-2.3}(\text{P}_{0.7-0.8}\text{Si}_{0.6-0.8}\text{S}_{0.1-0.3}\text{As}_{0-0.1})_{1.32-1.64}\text{O}_4$. Silicon is positively correlated with P ($R^2=0.7$). The EMPA elemental maps reveal homogeneous distribution of P, Si, Nd, Y and U in P-coffinite and Si-ningyoite.

These results suggest that coffinite-(i) in Bangombé is not the alteration product of uraninite. But, P-coffinite and Si-ningyoite precipitated at the expense of uraninite under reducing conditions. The lack of correlation between P and Y+REE in P-coffinite and Si-ningyoite implies that these minerals may consist of nano-scale intergrowths of coffinite and homogeneously distributed (Ca,U,Y,REE)-phosphates. This is supported by the elemental maps, as well as TEM results.

Noble gases in permafrost perennial groundwater springs, Fishing Branch River, Yukon, Canada

N. UTTING^{1*}, I.D. CLARK¹, W. AESCHBACH-HERTIG²
AND M. WIESER²

¹Department of Earth Science, University of Ottawa, 140
Louis Pasteur, Ottawa, Ontario K1N 6N5 Canada
(*correspondence: nicholas.utting@uottawa.ca)
(idclark@uottawa.ca)

²University of Heidelberg, Institute of Environmental Physics
Im Neuenheimer Feld 229, 69120 Heidelberg, Germany
(aeschbach@iup.uni-heidelberg.de,
martin.wieser@iup.uni-heidelberg.de)

There has been limited research on noble gases in permafrost terrain, with most research to date focusing on saline springs in the high arctic [1], and brines deep below the surface [2]. In this study noble gases have been used to better understand flow of perennial groundwater springs in permafrost terrain along the Fishing Branch River, Yukon, Canada. Noble gas samples have been collected from five groups of springs using diffusion samplers and copper tube samplers. Samples have been analysed for ³He, ⁴He, Ne, Ar, Kr and Xe. It is expected that groundwater springs will be a mix of perennial groundwater and active layer melting [3]. The R/R_a of these samples suggests that there are two groundwater sources with mixing between active layer water, river water and perennial groundwater. The perennial groundwater system has a lower R/R_a due to addition of crustal helium, while shallow active layer water will be dominated by ingrowth of ³He from tritium. Many samples are characterized by high excess air, which is likely due to recharge in the permafrost environment, with large water table changes and freeze thaw cycles.

[1] McKay *et al.* (2005). Polar Lakes, Streams, and Springs as Analogs for the Hydrological Cycle on Mars, *Water on Mars and Life, Advances in Astrobiology and Biogeophysics*. Springer, Berlin. [2] Greene (2005) *Noble Gases of the Canadian Shield from the Lupin and Con Mines, Canada, as indicators of deep groundwater flow dynamics and residence time*. M.Sc., University of Ottawa. [3] Clark & Lauriol (1997) *Arctic and Alpine Research* **2**, 240-252.

Relations between Mediterranean cyclones and African Monsoon from speleothems of Negev Desert, Israel

A. VAKS^{1,2,3}, M. BAR-MATTHEWS², A. AYALON²,
A. MATTHEWS³ AND A. FRUMKIN⁴

¹Department of Earth Sciences, University of Oxford, Parks
Road, Oxford OX13PR, UK

²Geological Survey of Israel, 30 Malkhey Israel Street, 95501
Jerusalem, Israel

³Institute of Earth Sciences, Hebrew University of Jerusalem,
91904 Jerusalem, Israel

⁴Department of Geography, Hebrew University of Jerusalem,
91905 Jerusalem, Israel

Carbonate cave deposits (speleothems) from the central and southern Negev Desert, southern Israel, were used to reconstruct the paleoclimate conditions on the northern boundary of Saharan-Arabian Desert. Speleothem deposition does not occur today in this arid to hyper arid region (150-30 mm/year), but the presence of speleothems in many caves indicates that humid conditions prevailed in the past.

Speleothems have been continuously deposited throughout glacial and interglacial intervals for at least the last 500 ka in the present-day Mediterranean climate zone of northern and central Israel (>350 mm/year). In contrast, in the central and southern Negev Desert only clusters of short humid episodes occurred, resulting in minor speleothem deposition during: interglacial Marine Isotopic Stage (MIS) 9 at 350-310 ka (Negev Humid Period (NHP)-4), glacial MIS-8 at 310-290 ka (NHP-3), interglacial MIS-7.3-7.1 at 225-185 ka (NHP-2), and NHP-1, which encompasses the transition between glacial MIS-6.1 and interglacial MIS-5.5, and interglacial MIS-5.5-5.4 at 142-109 ka.

Progressive thinning of the speleothem cross sections from the north to the south, speleothem $\delta^{18}\text{O}$ values and the δD values of speleothem fluid inclusions all indicate that the precipitation came from the Atlantic-Mediterranean cyclones.

The NHP were contemporaneous with periods of high Northern Hemisphere insolation with African monsoon index of 51 cal/cm²/day and higher. Contemporaneous Intensification of the Mediterranean cyclones and the African monsoon can possibly be explained by warming of subtropical Atlantic SSTs by the increased insolation. Higher SSTs weakened the Azorian High Pressure Cell, contributing to higher intensity of African Monsoon in the summer and decreasing NAO index in the winter, consequently intensifying the cyclonic activity above the Mediterranean Sea and northern margins of Saharan-Arabian Desert.