

Radiation damage evolution in nanocomposites

BLAS PEDRO UBERUAGA

Materials Science and Technology Division, Los Alamos
National Laboratory, Los Alamos, NM 87545;
correspondence: blas@lanl.gov

As nuclear energy systems are taken to higher levels of radiation damage, there is greater need to develop materials that can withstand that damage. Nanocomposites, nanomaterials comprised of both a high density of internal interfaces and second phases, are one promising avenue for such materials. Most work on nanomaterials has focused on the role of the interfaces as sinks of point defects. Here, motivated by a series of experimental studies on oxide composites, we examine the other component of nanocomposites, the dual phase nature of the material without the interfaces acting as defect sinks. We solve a reaction-diffusion model of defect evolution of simple composites under irradiation which depends on defect properties within each phase with no special behavior accounted for at the interface. We identify three regimes of steady-state defect behavior that depend on the relative thermodynamics and kinetics of the defects in the phases comprising the composite. Importantly, in one regime, defect populations are enhanced on one side of the interface and depleted on the other. Further, transient defect populations can exceed steady-state concentrations. We conclude that the evolution of irradiation-induced defects in one phase of the composite is strongly controlled by the defect properties of the other phase, offering a route to controlling defect evolution in these materials.

Magmatic processes revealed by heterogeneous crystal populations in a lamprophyre system

T. UBIDE^{1,2*}, C. GALÉ¹, P. LARREA¹, E. ARRANZ¹,
M.LAGO¹ AND J.R. WIJBRANS²

¹Universidad de Zaragoza, Spain (*correspondence: tubide@unizar.es)

²VU University Amsterdam, The Netherlands

Minerals respond texturally and compositionally to changing magmatic environments. We have studied a Cretaceous alkaline lamprophyre intrusion cropping out in the Catalonian Coastal Ranges in NE Spain [1] which includes macrocrysts and microcrysts of clinopyroxene and amphibole with complex zoning patterns. Mineral textures, compositional zoning, barometric estimates and geochronology provide insights into the magma plumbing system.

Macrocryst cores show inverse zoning patterns from more evolved to more primitive compositions. Therefore, they are not in equilibrium with the magma that hosts them and cannot be considered true phenocrysts. Rather, they are classified as antecrysts [2] recycled from earlier stages of the magma system. Macrocryst rims and microcrysts, in contrast, define an evolution from more primitive to more evolved compositions that can be related to progressive fractionation of the magma.

According to clinopyroxene barometry [3], macrocryst cores crystallised in a deep magma chamber (500-800 MPa) whereas macrocryst rims and microcrysts crystallised during the ascent and shallow emplacement of the magma below 50 MPa pressure. ⁴⁰Ar/³⁹Ar ages reveal a short timespan between the crystallisation of macrocrysts and microcrysts.

Our results reveal repeated injection and mixing of batches of a more primitive magma with the resident magma in a deep magma chamber, controlling the crystallisation of macrocryst cores (antecrysts). The last recharge event likely triggered the ascent of the magma to the emplacement level, carrying a significant amount of recycled crystals. The melt underwent fractionation during ascent and emplacement, controlling the composition of macrocryst rims and microcrysts.

This investigation highlights the need to carefully evaluate mineral zoning patterns and mineral-melt equilibrium in apparently simple porphyritic rocks.

[1] Ubide *et al.* (2012) *Lithos* **132-133**, 37-49. [2] Davidson *et al.* (2007) *Annu. Rev. Earth Planet. Sci.* **35**, 273-311. [3] Putirka (2008) *Rev. Mineral. Geochem.* **69**, 61-120.

Sedimentary organic matter variations in the Chukchi Borderland over the last 155 kyr

MASAO UCHIDA¹ AND STEPHAN RELLA²

¹16-2 onogawa tsukuba 305-0044, japan, uchidama@nies.go.jp

²16-2 onogawa tsukuba 305-0044, japan, stephanrella@gmail.com

Knowledge on past variability of sedimentary organic carbon in the Arctic Ocean is important to assess natural carbon cycling and transport processes related to global climate changes. However, the late Pleistocene oceanographic history of the Arctic is still poorly understood. In the present study we show sedimentary records of total organic carbon (TOC, $\delta^{13}C$), $CaCO_3$, benthic foraminiferal $\delta^{18}O$, molecular markers (BIT index) and the coarse grain size fraction from a piston core recovered from the northern Northwind Ridge in the far western Arctic Ocean, a region potentially sensitively responding to past variability in surface current regimes and sedimentary processes such as coastal erosion. An age model based on oxygen stratigraphy, radiocarbon dating and lithological constraints suggests that the piston core records paleoenvironmental changes of the last 155 kyr.

TOC shows orbital-scale increases and decreases that can be respectively correlated to the waxing and waning of large ice sheets dominating the Eurasian Arctic, suggesting advection of fine suspended matter derived from glacial erosion to the Northwind Ridge

by eastward flowing intermediate water and/or surface water and sea ice during cold episodes of the last two glacial interglacial cycles. At millennial scales, increases in TOC might correlate to a suite of Dansgaard-Oeschger Stadials between 120 and 45 ka before present (BP) indicating a possible response to abrupt northern hemispheric temperature changes. Between 70 and 45 ka BP, closures and openings of the Bering Strait could have additionally influenced TOC variability. $CaCO_3$ content tends to anti-correlate with TOC on both orbital and millennial time scales, which we interpret in terms of enhanced sediment advection from the carbonate rich Canadian Arctic via an extended Beaufort Gyre during warm periods of the last two glacial-interglacial cycles and increased organic carbon advection from the Siberian Arctic during cold periods when the Beaufort Gyre contracted.

Exploring fractionation models for some martian primary magmas

A. UDRY^{1*}, H. Y. MCSWEEN¹ AND J. B. BALTA¹

¹Planetary Geosciences Institute, Dept. of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996, USA. (*Correspondence: audry@utk.edu)

The martian surface is mainly composed of tholeiitic basalts [1] as well as some alkaline compositions and sediments derived from basalts. Two hypotheses have been proposed to explain the compositions of martian basalts: 1) melting of martian mantle under various conditions, forming primary magmas with diverse compositions [2], or 2) fractional crystallization of primary magmas, resulting in the various basaltic compositions [3]. On the Earth, the Moon, and the asteroid 4 Vesta, primary magmas are scarce, indicating that most magmas fractionated during ascent. This model should also be applicable for Mars.

We conducted hundreds of fractional crystallization calculations for four different martian primary magmas: 1) Humphrey, 2) Fastball, 3) Yamato-980459, and 4) nakhlite parental melts, using MELTS and pMELTS [4]. Previously, all calculations and experiments have been isobaric. Our results are the first calculations conducted on martian magmas under polybaric conditions. In addition, we investigated isobaric and polybaric calculations at various oxygen fugacities, water contents, and P-T paths for each primary magma. Our study shows that polybaric fractionation of primary magmas (except Y-98) leads to the formation of alkaline compositions if most of the crystallization occurs at high pressures but forms subalkaline compositions if magma undergoes fractionation during rapid ascent.

In addition to examining martian primary magma evolution, we investigated formation of three specific martian alkaline rock compositions: 1) Backstay, 2) Jake Matijevec, and 3) nakhlite intercumulus glass. Backstay and the nakhlite intercumulus glass compositions can be formed through fractional crystallization of tholeiitic primary magmas, with or without water, and with a primary magma held at high pressures. Jake Matijevec [5] likely formed from a metasomatized alkali-rich melt. Our results suggest that alkaline magmas on Mars are formed similarly as on Earth and may be more common than suggested by orbital surveys for alkaline rocks.

[1] McSween *et al.* (2009) *Science*, 324, 736- 739. [2] Baratoux *et al.* (2011) *Nature*, 472, 338-341. [3] McSween *et al.*, (2006) *J. Geophys. Res.* 111, E09S91. [4] Ghiorso and Sack (1995) *Contrib. Min. and Pet.*, 119, 197-212 [5] Stolper *et al.* (2013) LPSC XLIV, Abstract #1685.

Cause of the maximum S-MIF scatter in the late Archean: atmospheric organic sulfur and episodic volcanism

YUICHIRO UENO^{1,2*}, SEBASTIAN O. DANIELACHE³,
MASAFUMI SAITO¹, YOSHIKI ENDO¹
AND MATTHEW JOHNSON⁴

¹Earth & Planetary Sciences, Tokyo Institute of Technology, Japan. (ueno.y.ac@m.titech.ac.jp)

²Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, Japan

³Faculty of Science & Technology, Sophia University, Japan

⁴Copenhagen Center for Atmospheric Research, Department of Chemistry, University of Copenhagen, Denmark.

Sulfur Mass-Independent Fractionation (S-MIF) has been useful to monitor chemistry of the Earth's early atmosphere. In the latest Archean, from 2.7 to 2.5 Ga, $\Delta^{33}\text{S}$ values of sedimentary sulfides exhibit exceptionally large variation compared to older period. The maximum scatter of S-MIF may indicate anomalous chemistry of atmosphere or climatic system of the late Archean Earth, though the primary cause of the large MIF is still poorly understood. We have developed a sulfur isotopic model by improving atmospheric reaction model [1,2]. The improvements to our model includes the addition of hydrocarbon chemistry, chemical formation and deposition of organic sulfur haze, together with newly determined high-accuracy ultraviolet absorption cross sections of SO_2 isotopologues. Our model results suggest that after a volcanic injection of SO_2 into the Archean atmosphere, a significant fraction of the sulfur is converted into organic sulfur and could be accumulated in an atmosphere over a timescale of 10 years, if background atmosphere is reducing enough to yield hydrocarbon haze and volcanic sulfur input is large and episodic. Such model could explain the large $\Delta^{33}\text{S}$ preserved in sedimentary rocks. Moreover, isotopically fractionated two reservoirs (i.e. atmosphere and ocean) can be mixed episodically and thus possible to explain the observed small scale heterogeneity of S-MIF even within a hand specimen level. Preservation process of the S-MIF could have been more dynamical than previously thought.

[1] Danielache *et al.* (2008) *J Geophys Res* **113**, D17314. [2] Ueno *et al.* (2009) *PNAS* **106**, 14784-14789.

The relation between metasomatism and redox state of the upper mantle below the Massif Central, France

LAURA UENVER-THIELE¹, A. B. WOODLAND¹, H. DOWNES² AND R. ALTHERR³

¹ Institut für Geowissenschaften, Universität Frankfurt, Frankfurt, Germany (laura.uenver@online.de),

² School of Earth Sciences, Birkbeck College, University of London, London WC1E 7HX, UK

³ Institut für Geowissenschaften, Universität Heidelberg, 69120 Heidelberg, Germany

Several studies have demonstrated the existence of two geochemically and texturally distinct mantle domains lying north and south of $45^\circ 30'$, respectively [1,2]. These two domains are also reflected by differences in their redox state [3] and record different metasomatic overprints. The aim of this study is to combine redox and trace element data to more closely investigate these metasomatic processes at various length scales.

Preliminary trace element data indicate multiple types of enrichment in LREE, MREE and HSE. These different signatures occur regionally as well as locally, which implies variations in metasomatic style with depth. Most northern domain samples have high La/Nd (>10), but low Sm/Yb (<0.8) and $\log f\text{O}_2$ values $> \text{FMQ}+0.9$. The southern domain appears to have been affected by several different types of metasomatic overprints with variable intensity (e.g. high $(\text{Ce}/\text{Yb})_N$). Oxidation states are also a function of rock type, with harzburgites having $\log f\text{O}_2 \sim \text{FMQ}+1.0$ and lherzolites lying by $\sim \text{FMQ}+0.5$. The harzburgites appear to be more sensitive to changes in oxidation state, presumably due to their generally low spinel contents. The presence of small amounts of amphibole does not correlate with degree of enrichment or the highest $f\text{O}_2$ values. Investigation of how geochemical and redox heterogeneities are influenced by rock type and texture are currently underway.

[1] Downes H. *et al.* (2003) *Chem. Geol.*, 200, 71-87. [2] Lenoir, X. *et al.* (2000) *Earth Planet. Sci. Lett.* 181, 359-375. [3] Uenver-Thiele L. *et al.* (2013) EGU abstract 11398.

Detailed history of atmospheric pollution in South America as recorded by trace elements in the Quelccaya ice core

C. UGLIETTI¹, P. GABRIELLI^{1,2} AND L.G. THOMPSON^{1,2}

¹ Byrd Polar Research Center, 108 Scott Hall, The Ohio State University, 1090 Carmack Road, Columbus, OH 43210, USA (ugliettichiara@gmail.com)

² School of Earth Sciences, The Ohio State University, 125 South Oval Mall, Columbus, OH 43210, USA (gabrielli.1@osu.edu)

Reconstructions of past trace-metal deposition are extremely important to address questions linked to changes in land-use, climate, aeolian dust and to identify spatial patterns and temporal trends in global trace-metal associated with anthropogenic activities. The tropical Andes are particularly interesting because they host a long mining history associated with mineral exploitation and environmental impacts. The glacio-chemical record preserved in the ice of the Quelccaya ice cap, located within the southern Peruvian Andes offers a unique opportunity to geochemically constrain the composition of the tropical atmosphere at sub-annual resolution through time. Two ice cores were retrieved from the ice cap in 2003 (Summit Dome core, (QSD; 5670 m asl, 168.68 m) and North Dome core (QND; 5600 m asl, 128.57 m). Determination of twenty trace elements (Ag, Al, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Sn, Ti, Tl, U, V, and Zn) was performed by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS, Element 2) over the first 120 m of the QND core, spanning the time period between 1990 AD and 1500 AD. As, Bi, Cd, Cu, Mn, Mo, Pb and Zn show different increases in concentration and crustal enrichment factors over this time period pointing to varying anthropogenic sources.

Geochemistry of urban soils in Karlstad, central Sweden – preliminary results

J. UHLBÄCK¹, A. LADENBERGER¹, M. ANDERSSON¹
AND M. SADEGHI¹

¹Geological Survey of Sweden, Box 670, S-751 28 Uppsala, Sweden (*correspondence: anna.ladenberger@sgu.se)

As a part of the European project URGE (Urban Geochemistry), in collaboration with EuroGeoSurveys Geochemistry Expert Group (EGS-GEG), surface soils were surveyed in the urban area of the municipality Karlstad in central Sweden to assess geochemical patterns of potentially toxic metals and other elements that can be considered dangerous at elevated concentrations.

306 surface (<10 cm depth) soil samples were collected from Karlstad town and analysed with aqua regia (AR) digestion by ICP-MS. The results show elevated concentrations of Cd, Cu, Pb, Sb and Zn in industrial parts of the town and in the harbour, while playgrounds, residential districts and recreation areas show lower concentrations. Broadly defined greenfields show more variation in metal concentrations, most likely due to the wider spread of potential sample sites in this category. The results display a mixed and complicated relationship between the geological background and anthropogenic overprint, with elevated concentrations in areas with historical and present industrial activity. The geochemical patterns of Ni, Cr and Co are similar and possibly related to the presence of mafic rocks within the extent of the town (especially in the southern part of Karlstad). Elevated As levels occur randomly in greenfield areas indicating a rather natural origin of these anomalies. Higher concentrations of Pb, Cd and Ni in the city centre can be related to traffic. High Cu and Zn contents in the town's central parts point to the long-term use of copper-zinc construction details in buildings, e.g. gutters and roof elements. Elevated Hg concentrations in several places by the Klara river may indicate the pollution related to sewage and fertilizers and affinity of Hg to bind to organic matter-rich bank sediments.

The results from this study can be further used by the local authorities for future planning of the infrastructure and slum-clearance of contaminated land. Potential health risks for inhabitants who reside and work in contaminated areas can also be assessed, with the aim to specify and inform the public about possible precautionary measures.

Structural-diagenetic evolution of fractures in folds: A TGS example from the Alberta Foothills, Canada

E. UKAR*, P. EICHHUBL AND A. FALL

The University of Texas at Austin, Bureau of Economic Geology, PO Box X, Austin, TX 78713

(*correspondence: esti.ukar@beg.utexas.edu)

The late Jurassic-early Cretaceous Nikanassin formation is generally characterized as a tight gas sandstone formation with submillidarcy values of permeability and porosities typically less than 6% [1]. However, the Nikanassin produces gas at commercial rates where it contains a network of open fractures. But exploration and development outcomes are mixed, underlining the necessity for a better understanding and characterization of the more fractured and potentially more productive regions [2].

A unique combined outcrop and core study of fractures associated with three reservoir-scale anticlines reveals the presence of two main fracture sets in all three mesostructures: fracture set one is perpendicular to the fold axis, whereas fracture set two is parallel. Both sets have an associated conjugate oblique fracture set. Scanline data indicate a higher fracture intensity in the steeply-dipping limbs of the folds than in the shallower-dipping limbs. Cathodoluminescence images of cemented fractures reveal several generations of quartz and ankerite cement that are synkinematic and postkinematic relative to fracture opening. Based on homogenization temperatures of two-phase aqueous inclusions in crack-seal cement, synkinematic fracture opening and cement precipitation occurred at or near maximum burial in core samples (190-210°), and during exhumation in outcrop samples (120-160°).

Structural models constructed using MOVE [3] predict a higher strain accumulation in the steep limb of the Sternie Creek Anticline than in the fold hinge and shallow limb. Models also predict an early opening of fracture set 1, which is in accordance with the general observation that set 2 cross-cuts set 1 in outcrop. Opening of most fractures probably occurred during regional folding at the end of the Laramide orogeny.

[1] Solano *et al.* (2011) *SPE Res. Eval. & Eng.* **14**, 357-376

[2] Hayes (2009) *Search and Discovery* article #10182 [3] MOVE Midland Valley Structural Restoration Software

Anammox in an ammonium-impacted groundwater aquifer

ANNE ULDAHL^{1*}, BO THAMDRUP²
AND RASMUS JAKOBSEN³

¹DTU Environment, Technical University of Denmark. Miljøvej, Building 113, DK-2800 Kgs. Lyngby. (*correspondence: annu@env.dtu.dk)

²NordCEE and Institute of Biology, University of Southern Denmark. Campusvej 55, DK-5230 Odense M.

³GEUS, Geological Survey of Denmark and Greenland. Oestervoldgade 10, DK-3500 Copenhagen K.

The novel anaerobic ammonium oxidation pathway (anammox) is today recognized as an important sink for reactive N, removing biologically available N in the form of ammonium and nitrite to the gaseous N₂, providing a competition to the dissimilatory nitrite reduction by denitrifiers. Anammox activity and the responsible bacteria are currently demonstrated in a wide range of ecosystems, however; the knowledge about anammox in freshwater systems, like ammonium-impacted groundwater aquifers, is still scarce. With the necessary electron donors and acceptors present in the groundwater system, the activity and abundance of anammox bacteria could be of significant importance since biologically available N, resulting from anthropogenic sources, is a major threat to groundwater quality.

We hypothesize that the anammox process occurs in a contaminated groundwater system, when NO₂⁻ and NH₄⁺ are present under low oxygen conditions. Isotope-based methods were used to quantify anammox activity through the isotope pairing technique: two-meter sediment cores were collected from a groundwater system adjacent to the abandoned landfill site Risby, Denmark; chosen intervals were sectioned and incubated anaerobically as sediment slurries. The production of ²⁹N₂ and ³⁰N₂ was monitored over time after addition of labelled N and unlabelled N as: ¹⁵NO₃⁻ + ¹⁴NH₄⁺ for detecting anammox, denitrification (nitrite reduction to N₂) and DNRA (dissimilatory reduction of ammonium) and with ¹⁵NH₄⁺ + ¹⁴NO₃⁻ for detecting anammox production. Our results show that both anammox and DNRA are active, with denitrification as the dominating pathway.

Preservation potential of $\delta^7\text{Li}$ values in Mesozoic calcite fossils

C.V. ULLMANN^{*1,2}, H.J. CAMPBELL³, R. FREI¹, S.P. HESSELBO², P.A.E. POGGE VON STRANDMANN² AND C. KORTE¹

¹University of Copenhagen, IGN, Øster Voldgade 10, 1350 Copenhagen, Denmark

(*correspondence: c.v.ullmann@gmx.net)

²University of Oxford, Department of Earth Sciences, South Parks Road, Oxford OX1 3AN, United Kingdom

³GNS Science, 1 Fairway Drive, Avalon 5010, New Zealand

Lithium isotopes of fossil carbonates are a promising proxy for determining the intensity of silicate weathering. Here we use elemental and isotopic trends in diagenetically altered Late Jurassic belemnites (*Belemnopsis* sp. and *Hibolithes* sp.) from New Zealand to see if meaningful $\delta^7\text{Li}$ values are preserved in fossil calcites over time spans of > 100 m.y.

The parts of the belemnite rostra that are most altered are characterized by low $\delta^{18}\text{O}$ reaching -12‰ and moderate decreases in $\delta^{13}\text{C}$ (down to -2‰), coupled with high Mn/Ca ratios reaching 4.6 mmol/mol. Both, Sr/Ca ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were found to decrease with progressive alteration. The direction and magnitude of the trends indicate one main diagenetic phase.

Altered materials show variable $\delta^7\text{Li}$ values between +24 and +40‰, while $\delta^7\text{Li}$ values of the sedimentary matrix are -5‰. $\delta^7\text{Li}$ values of best preserved belemnites are $+27 \pm 1$ ‰ (2 sd, n = 5), pointing to a Late Jurassic seawater $\delta^7\text{Li}$ of ~29-32‰, compatible with the modern value of 31‰. Despite burial down to ~4 km, and thus elevated temperatures, uniform $\delta^7\text{Li}$ values in the well-preserved fossil calcites, and strong isotopic gradients between fossil calcite and sediments have been maintained. This suggests that primary $\delta^7\text{Li}$ values can be preserved over geological timescales.

Recent views on lamprophyric melilitic rocks (polzenites) of the Bohemian Massif

JAROMÍR ULRYCH^{1*} AND LUKÁŠ KRMÍČEK²

¹Institute of Geology v.v.i., Academy of Sciences of the Czech Republic, Rozvojová 269, CZ-165 00 Praha 6, Czech Rep. (*correspondence: Ulrych@gli.cas.cz)

²Brno University of Technology, Faculty of Civil Engineering, Veveří 95, CZ-602 00 Brno, Czech Rep.

The easternmost part of the Cenozoic Volcanic Province of western and central Europe includes rare occurrences of Late Cretaceous to Paleocene (70 to 59 Ma) ultramafic melilitic and melilite-bearing rocks. These rock suites, related to the initial stage of rifting of the Bohemian Massif, occur in the shoulder blocks of the Ohře/Eger Rift zone. Here, in the Ploučnice (Polzen) River area, a group of clinopyroxene-free melilitic rocks - polzenites - was defined by K.H. Scheumann in 1913. He recognized three principal petrographic types of polzenite: Vesec, Modlibohov and Luhov type. Inspecting the petrography of the separate types we find that the Vesec type is represented by polzenite s.s. only (olivine + melilite + nepheline + phlogopite + spinels + calcite ± monticellite, hauyne, perovskite, apatite mineral associations), whereas the Modlibohov type is transitional to the Luhov type representing a clinopyroxene-bearing melilitic rock – alnöite, as defined by H. Rosenbusch in 1887.

Regarding the classification of polzenites, there are currently two petrographic approaches. According to the first view polzenites represent only lamprophyric, i.e. volatile-rich, facies [1] of melilite-bearing group of rocks and can be added as a special petrographic type into this group. According to the second view, polzenites belong to an individual group of ultramafic lamprophyres, however they are considered by some scientists as a more felsic variant of alnöite [2]. With respect to the petrography of clinopyroxene-free polzenite (the Vesec type) for which values of Mg# between 74 and 78 are typical, polzenite can be considered a valid end-member of the ultramafic lamprophyre group.

Acknowledgements. This work was supported by the project "EXCELLENT TEAMS" at BUT; registration number CZ.1.07/2.3.00/30.0005.

[1] Mitchell (1994) *Miner. Petrol.* **51**, 137–146. [2] Tappe *et al.* (2005) *J. Petrol.* **46**, 1893–1900.

Forceful Carbonation of Serpentine

O. I. ULVEN*, H. AUSTRHEIM
AND A. MALTHER-SØRENSSEN

Physics of Geological Processes, University of Oslo, 0316
Oslo, Norway (*Correspondence: o.i.ulven@fys.uio.no)

Mineral carbonation has been suggested as an option for long term sequestration of anthropogenic CO₂[1]. It is in this respect critical to know whether the growth of carbonate minerals will clog pore space, and thus limit further transport of CO₂ into the rock, or whether the carbonate growth will exert enough stress on the host rock to make it fracture, thus making new fluid pathways.

In this work, we perform a numerical study of natural field examples of growth of carbonate minerals in serpentine, and we use a discrete model to reproduce observed structures.

We achieve an improved understanding of the process of mineral carbonation and the feedback on rock deformation, thus improving our ability to determine whether industrial scale mineral carbonation is a viable option for long term storage of CO₂.

[1] Kelemen, P.B, and Matter, J.(2008), Proceedings of the National Academy of Sciences of the United States of America, Vol. 105(45): pp. 17295-17300

Limited releases of U and Tc from Hanford tank residual wastes

WOYONG UM^{1,2,*} AND KIRK J. CANTRELL¹

¹Pacific Northwest National Laboratory, Richland, WA, USA
²Pohang Univ. of Sci. and Technol., Pohang, South Korea
wooyong.um@pnnl.gov (* presenting author)

Most of the Hanford Tank wastes in Washington, USA are expected to be retrieved, stabilized in an appropriate waste form and then disposed in a repository. Small amounts of residual wastes are expected to remain at the bottom of the tanks in a layer no more than 2.54 cm thick as slurry of solid precipitates. The current final stage of tank closure is planned to consist of the addition of cement or grout to stabilize the remaining wastes and tank structure. In this study, three different chemical treatment methods (lime [Ca(OH)₂] addition, an in-situ Ceramicrete based on chemically bonded phosphate ceramics, and a ferrous Iron/Goethite treatment) were tested for their ability to stabilize residual Hanford C-202 tank wastes for reducing contaminant release of Tc and U in particular because they are key groundwater risk drivers.

Leaching tests were conducted using a single-pass flow-through test (SPFT) system with 0.005 M Ca(OH)₂ solution for untreated tank sample and C-202 wastes treated with three different chemical treatments. Technetium concentrations in leachates from tank C-202 residual waste treated with the Ca(OH)₂, Ceramicrete, and Goethite methods are shown in Fig.1. All three treatments methods effectively reduced the leachable Tc concentrations as well as U to well below untreated waste as a result of formation of insoluble secondary precipitates which can behave like mineral coatings.

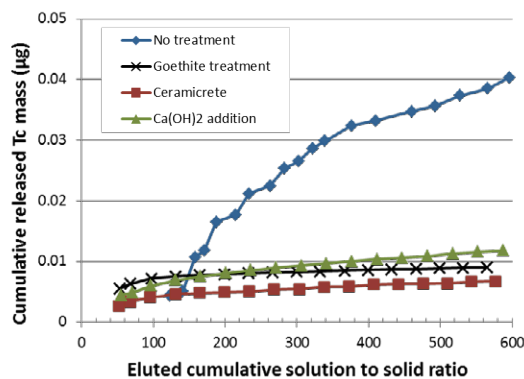


Fig. 1. Released cumulative Tc amounts from the residual wastes.

This innovative approach has the potential to revolutionize Hanford's tank retrieval processes, by allowing larger volumes of residual waste to be left inside tanks while providing an acceptably low level of risk with respect to contaminant release as well as significant cost savings.

Chemical composition of detrital spinel from Eastern Chugoku and Northern kinki of Sangun zone, Southwest Japan.

TOMOYUKI UMEDA¹ AND ICHIRO MATSUMOTO¹

¹Faculty of Education, Shimane University, Matsue, Japan, umedatomoyuki@gmail.com (*presenting author) chromim@edu.shimane-u.ac.jp

Geochemical characteristics of chromian spinel from ultramafic rocks and chromitites in Sangun zone of Central chugoku district have become clear gradually by recent many studies [1,2]. Especially, petrogenesis of chromitite formation [3] and exfoliation for chromitite [4] came to be advanced from these works. However, ultramafic complexes in Sangun zone distribute not only central chugoku district but also from eastern chugoku to northern kinki districts, which are called Wakasa, Sekinomiya, Izushi, Oeyama complexes respectively. Chromitite pods and chromite mines (now closed) also existed in these district. Detailed research of chromian spinel from ultramafic rocks and chromitite in this district is not done sufficiently, and there is the required for a geochemical description for understand origin and petrogenesis of ultramafic rocks and chromitite. However ultramafic rocks in the Sangun zone of these district are also strongly altered and serpentinized. Then we use detrital chromian spinel from the stream sediment, in this study. This is the first report of chemical composition of detrital chromian spinel from ultramafic rocks and chromitite in Sangun zone of from eastern chugoku to northern kinki district.

Cr#(=Cr/Cr+Al) of detrital chromian spinel from Sekinomiya complex varies from 0.43 to 0.56. Cr# of those from Izushi complex varies from 0.36 to 0.56 (mainly 0.43 to 0.50). Cr# of those from Oeyama complex varies from 0.43 to 0.69. That is, Cr# of those from eastern chugoku to northern kinki district overlap with the Cr# (0.4 to 0.6) of detrital spinel from central chugoku district. In addition, We found chromitite boulder in Oeyama complex, and show that Cr# of chromian spinel varies from 0.38 to 0.43, that is the most High-Al podiform chromitite in Japan. This is significant petrological description, indicating involvement of both Al-rich melt and of fertile harzburgite.

[1] Arai (1980): *J. Petrol.*, 21, 141-165. [2] Matsumoto *et al.* (1995): *J.Jpn.Assoc.Mineral.Petrol.Econ.Geol.*, 90, 333-338. [3] Arai and Yurimoto (1994): *Econ. Geol.*, 89, 1279-1288. [4] Matsumoto and Arai (1997): *Resource-Geology*, 47, 189-199.

Petrological Implications of Temporal and Spatial Variations in Magma Chemistry of the Quaternary Tendurek Shield Volcano, Eastern Anatolian Collision Zone, Turkey

E. UNAL^{1*}, M. KESKIN², V.A. LEBEDEV³, ANDREY V. CHUGAEV³ AND E.V. SHARKOV³

¹YYU, Dept. of Geol. Engineering, Zeve Campus, Van, Turkey (*correspondence: esinunal@yyu.edu.tr)

²Istanbul Univ., Dept. of Geol. Engineering, Avcilar, Istanbul, Turkey (keskin@istanbul.edu.tr)

³RAS, IGEM, Staromonetny per., 35, Moscow, Russia

The Quaternary Tendürek Volcano is one of the largest eruption centers of the Eastern Anatolia with a summit elevation of 3538 m and a footprint area of 650 km². It is a shield volcano consisting of lavas ranging in composition from tephrites through benmoreites/phonolites to trachytes. The young volcanism of the region is thought to be related to the continent-continent collision taken place after the closure of the Neo-Tethys Ocean. The Tendürek volcano is of special importance, because it is one of the rare places in Eastern Anatolia where calc-alkaline and potassic alkaline volcanism coexisted.

Lavas of the Tendürek volcano are classified on the SiO₂ versus K₂O diagram as medium K / high K and shoshonitic series. Results of our FC, AFC and EC-AFC modelings indicate that the Tendürek lavas were influenced by crustal contamination and fractional crystallization. Medium to high potassic basalts, trachy-basalts, tephrites and basaltic-trachyandesites basically follow a partial melting trend on La vs. La/Yb diagram in contrast to the trachy-andesites, phonotephrites, tephriphonolites, phonolites, and trachytes of the shoshonitic series aligning along a fractional crystallization trend. The high-SiO₂ phonolitic lavas have a more pronounced enrichment in incompatible elements, such as Rb, Th, La and Nb, in comparison to those in the other shoshonitic rocks. The aforementioned differences in the chemical compositions of these two groups of shoshonitic rocks may reflect variations in the fractional crystallization process which involved clinopyroxene and plagioclase during the petrogenesis of the potassic rocks.

According to our melting model, primitive magma of the Tendürek lavas were derived from mixing of the spinel and garnet peridotite melts with different melting degrees ranging between 1 - 3%.

Possible link between CO₂ degassing and climate change in SW Turkey

E. ÜNAL-İMER^{1*}, I.T. UYSAL¹, J. SHULMEISTER¹
AND J.X. ZHAO¹

¹The University of Queensland, Brisbane, QLD, 4072,
AUSTRALIA (*correspondence: e.unal@uq.edu.au)

High-pressure CO₂-rich fluids can trigger fault activity by reducing the shear stress [1]. Subsurface meteoric water at crustal depths of 10–15 km, mainly contributed by local rainfall sourced groundwater, may be the major fluid source in large-scale continental extensional areas [2]. Carbonate vein deposits could precipitate from such CO₂-rich, deeply circulated overpressurised meteoric water within intensely-fractured/faulted rocks along active normal fault zones, within a rapidly extending region in SW Turkey [3,4,5] sub-samples of such vein calcites were investigated by advanced U-series dating and O-isotope analyses. The U-series ages show that calcite vein formations occurred largely during lower solar insolation (summer) periods in the Late Pleistocene in this region. These are interpreted as the periods of elevated effective precipitation, which could be responsible for fluid overpressures achieved by either increasing absolute or seasonal precipitation or by reducing evapotranspiration. Although full glacial periods are commonly associated with dry climatic conditions, regional conditions can vary. We suggest that the Eastern Mediterranean basin including Turkey was relatively wet under low to transitional insolation regimes, specifically, during the Last Glacial Maximum. This is likely a response to southerly-shifted westerly wind flow in the Northern Hemisphere bringing moisture supply over the study area. Further, the trend of δ¹⁸O values plotted against U-series ages of vein calcites demonstrate possible responses to either climate variability or seismicity-related fluid exchange mechanisms on mm scale.

It is possible to correlate fault activity recorded by co-seismic vein calcites as a product of CO₂ degassing and local climate controlling the effective precipitation. This means that seismic hazard can be linked to changing climatic conditions in the region. Consequently, earthquake clusters in SW Turkey may be considered to be climate-related and a function of the increased availability of fluids during cool to cold climate periods.

[1] Hickman *et al.* (1995) *J. Geophys. Res.* **100**, 12,812–12,831. [2] Wickham *et al.* (1993) *Geology* **21**, 81–84. [3] Uysal *et al.* (2009) *Chem. Geol.* **265**, 442–454. [4] Uysal *et al.* (2011) *EPSL* **303**, 84–96. [5] De Filippis *et al.* (2012) *Geol. Soc. Am. Bull.* **124**, 1629–1645.

Microbial corrosion of steel in Toarcian argillite: Influence of metabolisms and biofilms

L. URIOS^{1*}, A. PEREZ⁴, C. WITTEBROODT³, F. MERCIER⁴,
M. FLACHET², F. MARSAL², D. NEFF, M. MAGOT¹
AND P. DILLMANN⁴

¹Université de Pau et des Pays de l'Adour, IPREM EEM UMR 5254, IBEAS, 64013 PAU, France, (*presenting author, laurent.urios@univ-pau.fr)

²IRSN, PRP-DGE/SEDRAN/BERIS, B.P. 17, 92262 Fontenay aux Roses Cedex, France (margot.flachet@irsn.fr)

³IRSN, PRP-DGE/SRTG/LETIS, B.P. 17, 92262 Fontenay aux Roses Cedex, France (charles.wittebroodt@irsn.fr)

⁴SIS2M/LAPA, CEA/CNRS UMR 3299, 91191 Gif-sur-Yvette Cedex, France (philippe.dillmann@cea.fr)

In the context of geological disposal of radioactive waste in clayey formations, the consequences of a microbial activity are of concern regarding the corrosion of metallic materials. Actually microbial life has been highlighted in argillaceous formations [1]. Sulfate- and iron-reducing bacteria, as well as bacteria able to develop at high temperatures have been detected in Tournemire¹ (Toarcian argillite) [2]. They can grow at the interfaces between steel and argillite in a short period compared with planned durations of disposal. Such bacteria may influence corrosion [3], that may cause a premature loss of containment of metallic barriers. The formation of biofilms may also lead to environmental modifications at the biofilm/metal interface that may further increase corrosion rates [4]. Thus, an experimental setup was designed to understand the conditions favoring the formation of biofilm and the impact of microorganisms on steel corrosion.

A synthetic solution representative of the Tournemire pore water percolated through cells containing steel coupons placed in contact with Tournemire argillite. Various environmental conditions likely to prevail in a repository were tested (anoxic or oxic conditions, 25°C or 50°C). A mix of strains able to form biofilms and sulfate- and iron-reducing bacteria, each present in Tournemire argillite, has been inoculated. Cells were dismantled after 1, 4 and 8 months to establish a chronology of the involved processes. Analyses of outgoing water chemistry provided indications on mechanisms occurring within the cells. Observations of the steel surface were made using Field Emission Scanning Electron Microscopy and Raman spectroscopy. Molecular characterization of the microbial diversity was used to determine which species are responsible for corrosion.

¹ IRSN's experimental platform

[1] Urios *et al.* (2012) *Appl. Geochem.* **27**, 1442-1450. [2] Urios *et al.* (2013) *Geomicrobiol. J.* **30**, 442-453. [3] Herrera & Videla (2009) *Int. Biodeter. Biodegrad.* **63**, 891-895. [4] Little *et al.* (1991) *Int. Mater. Rev.* **36**, 253-272.

Assesing iron and oxygen isotope homogeneity in garnets

M. UROSEVIC¹, O. NEBEL¹, E.C. PETERSON²,
J.A. PADRÓN-NAVARTA^{1,3} AND D. RUBATTO¹

¹Research School of Earth Sciences, The Australian National University, Canberra, Australia

²Mineralogy, Technology and Innovation, Rio Tinto, Melbourne, Australia

³Géosciences Montpellier, Univ. Montpellier 2 & CNRS, 34095 Montpellier, France

Garnet is a key mineral for (i) dating metamorphic processes in the crust, (ii) tracing P-T conditions in the upper mantle, and (iii) understanding porphyry, skarn and epithermal ore systems. All of these geotectonic settings and associated processes are related to mass transfer of elements in fluids or melts. Detailed knowledge of the redox state under which such processes occur (often referred to as fO_2) and/or the source of fluids is crucial for the study of mass transfer in rock forming processes in crust and mantle.

Here we assess three natural garnets for their major, trace and O-Fe isotope budget in search of suitable standards and constraints on processes controlling their isotope systematics. One garnet from Kakanui, New Zealand (KAK) and two from Erongo, Namibia (ERO-R and ERO-G) are analysed. KAK is a xenocryst pyrope-rich garnet ($Alm_{22-23}Prp_{62-63}Grss_{12}And_2Spss_1$) from mantle-derived alkaline melt. ERO-R is an igneous almandine-rich garnet ($Alm_{64-65}Prp_{6-7}Grss_1And_{<1}Spss_{28-29}$) from a migmatitic vein with negligible proportion of Fe^{3+} . ERO-G is a hydrothermal highly zoned andradite-grossular-rich garnet ($Prp_{<1}Grss_{22-65}And_{32-77}Spss_{1-2}$) with all Fe as Fe^{3+} .

KAK is homogeneous in major and trace elements and in oxygen isotopes at the microscale with $\delta^{18}O \sim 5.3$. Its $\delta^{57}Fe_{(IRMM-014)} = +0.09 \pm 0.01$ is slightly elevated compared to average depleted mantle. Oxygen and Fe isotopes are homogeneous in ERO-R with $\delta^{18}O \sim 8.5$ and $\delta^{57}Fe = +0.11 \pm 0.06$, respectively. ERO-G garnet grains are zoned in oxygen composition with a variation from core to rim between ~ 13 and ~ 11 ‰, which coincides with the growth zoning pattern in Grss-Andr observed in BSE images. Accordingly, their heavy $\delta^{57}Fe$ vary from +0.6 to +0.9. Trace elements composition of ERO-G garnet is highly variable.

Based on our preliminary results KAK and ERO-R appear to be suitable standards for coupled Fe-O isotope analysis. Garnet O isotopes are in line with the source of the sample (mantle versus crust). Fe isotopes strongly correspond to Fe^{3+}/Fe^{2+} and may thus be a sensitive redox proxy in garnet.

Discovery of a Triassic magmatic arc source for the Permo-Triassic Karakaya subduction complex, NW Turkey

P. AYDA USTAÖMER^{1*}, TIMUR USTAÖMER², AXEL GERDES³, ALASTAIR H.F. ROBERTSON⁴
AND GERNOLD ZULAUF³

^{1*}Yıldız Teknik Üniversitesi, ustaomer@yildiz.edu.tr

²Istanbul Üniversitesi, Turkey

³Goethe-University, Frankfurt, Germany

⁴University of Edinburgh, U.K.

The Permo-Triassic Karakaya Complex is well explained by northward subduction of Palaeotethys but until now no corresponding magmatic arc has been identified in the region. With the aim of determining the compositions and ages of the source units, ten sandstone samples were collected from the mappably distinct Ortaoba, Hodul, Kendirli and Orhanlar Units. Zircon grains were extracted from these sandstones and >1300 were dated by the U-Pb method and subsequently analysed for the Lu-Hf isotopic compositions by LA-MC-ICP-MS at Goethe University, Frankfurt. The U-Pb-Hf isotope systematics are indicative of two different sediment provenances. The first, represented by the Ortaoba, Hodul and Kendirli Units, is dominated by igneous rocks of Triassic (250-220 Ma), Early Carboniferous-Early Permian (290-340 Ma) and Early to Mid-Devonian (385-400 Ma) ages. The second provenance, represented by the Orhanlar Unit, is indicative of derivation from a peri-Gondwanan terrane. In case of the first provenance, the Devonian and Carboniferous source rocks exhibit intermediate $\epsilon Hf(t)$ values (-11 to -3), consistent with the formation at a continental margin where juvenile mantle-derived magmas mixed with (recycled) old crust having Palaeoproterozoic Hf model ages. In contrast, the Triassic arc magma exhibits higher $\epsilon Hf(t)$ values (-6 to +6), consistent with the mixing of juvenile mantle-derived melts with (recycled) old crust perhaps somewhat rejuvenated during the Cadomian period. We have therefore identified a Triassic magmatic arc as predicted by the interpretation of the Karakaya Complex as an accretionary complex related to northward subduction (Carboniferous and Devonian granites are already well documented in NW Turkey). Possible explanations for the lack of any outcrop of the source magmatic arc are that it was later subducted or the Karakaya Complex was displaced laterally from its source arc (both post 220 Ma). Strike-slip displacement (driven by oblique subduction?) can also explain the presence of two different sandstone source areas as indicated by the combined U-Pb-Hf isotope and supporting petrographic data.

Multiple fluid events and metal mobility associated with formation of IOCG-type mineralisation in Gawler Craton

Y. UVAROVA^{1,2*}, J. CLEVERLEY^{1,2} AND R. HOUGH¹

¹CSIRO Earth and Resource Engineering, ARRC, Kensington, WA 6151 Australia (*correspondence:

Yulia.Uvarova@csiro.au)

²Deep Exploration Technologies CRC

The Gawler Craton, in South Australia, is host to the giant Olympic Dam deposit and a number of other economic to subeconomic iron oxide-copper-gold (IOCG) prospects including Prominent Hill, Oak Dam, Wirrda Well, Acropolis, Punt Hill, and Carrapateena. Several genetic models have been proposed for the formation of IOCG mineralisation in the Craton, but little is known about the source of metals and sulfur, and mechanisms of their transport and deposition.

Geologic and petrographic studies on IOCG prospects in the Olympic Dam district (Emmie Bluff, Canegrass, Cocky Swamp and Dromedary Dam) indicate several stages of fluid activity. Subeconomic Cu-Au mineralisation at these prospects is associated with the hematite-chlorite-sericite alteration with chalcopyrite commonly replacing pre-existing pyrite. With the use of cutting-edge Synchrotron X-ray Fluorescence Microscopy and Field Emission Gun Scanning Electron Microscopy it was shown for the first time that subeconomic IOCG mineralisation in the Gawler Craton was affected by a late fluid event, which resulted in partial dissolution of Cu mineralisation and transport of Cu in the form of chloride complexes. Patchy chlorite associated with the late alteration of chalcopyrite hosts a previously undescribed in IOCG rocks Cu-Cl phase. This Cu-Cl phase is interpreted to be a by-product of chalcopyrite partial dissolution and contains minor Zr, Y and U. The fluids must therefore have been rich in chlorine to mobilise Cu, and probably fluorine, as they were carrying relatively immobile Zr, Y and U which become mobile in the presence of fluoride complexes. This might be an indication of remobilisation and re-deposition of Cu along with other metals elsewhere in the district and could have implications for a possible metal source for the nearby Cu-Au deposits.

Understanding the role of Phanerozoic and active tectonics in generating geothermal resources in central Australia

I. T. UYSAL^{1*}, U. RING², AND A. W. MIDDLETON¹

¹University of Queensland, Queensland 4072, Australia¹

²Stockholm University, Stockholm 106 91, Sweden

(*correspondence: t.uysal@uq.edu.au)

Central Australia has a significant potential for geothermal development. Recent He and C isotope studies of volatiles from artesian waters suggest mantle-derived fluid reservoirs as a source of the geothermal resources [1], rather than radioactive heat production in the basement granitic rocks as widely believed. In conjunction with isotopic data of the volatiles, our structural geological field observations suggest that geothermal systems in central Australia preferentially occur in areas of deformation-enhanced permeability and deep mantle fluid production. To this end, we performed comprehensive isotopic dating studies (Rb–Sr, Ar–Ar and U-series) to understand the role of Phanerozoic and neotectonic deformations in permeability production and stable isotope tracing to determine the source of fluids in the geothermal reservoirs. Isotopic dating results and stable isotope geochemistry of hydrothermal minerals in basement rocks are interpreted as indicating that Cretaceous extensional tectonic events controlled the thermal history of central-eastern Australian basins and distribution of fracture zones allowing recent uprise of hot mantle fluids. Areas affected by Cretaceous tectonics are characterised by significantly high temperatures (>250°C) at 5 km depth [2] and distinctive geophysical anomalies [3]. Our field studies show that pre-existing faults were reactivated neotectonically and controlled the formation of late Quaternary carbonate vein and breccia deposits, which formed as hydro-fractures during CO₂-rich fluid overpressure, analogous to similar deposits in seismically active geothermal systems worldwide [4]. δ¹³C values of the carbonates are consistent with CO₂ derived from a mantle source. High precision U-series dating of carbonate veins suggests that the release of the pressurised CO₂ occurred intermittently from 35.9 ± 0.15 ka to 1.2 ± 0.02 ka, possibly in association with mantle degassing in response to seismicity.

[1] Italiano. *et al.* (2013), Submitted to *Chemical Geology*. [2] Chopra and Holgate (2005), Proceedings World Geothermal Congress 2005. [3] Saygin and Kennett (2012), *Journal of Geophysical Research* 117, B01304. [4] Uysal *et al.* (2009), *Chemical Geology* 265, 442-454.

Production of The Sodium Sulphate from Acıgöl by Solution Mining Method, Denizli, TURKEY

SERENA UZASCI SULTANYAN¹, SALIH BURAK
KARABEL¹, DEMET KIRAN YILDIRIM¹, MURAT
BUDAKOĞLU¹, MUHITTIN KARAMAN¹
AND MUSTAFA KUMRAL¹

¹Istanbul Technical University, Department of Geological
Engineering, 34469, Istanbul, TURKEY

Sodium sulphate is used widespread in industry. Common usage areas are paper, glass, detergent, textile, and chemical industries. In this study production of the Na₂SO₄ from the lakes by solution mining method has been examined. Evaporites and their usage areas, evaporite deposits in nature and types of it and production types of the sodium sulphate and detailed report about the information about the solution mining method and information of the Acıgöl Lake and production examples in it.

Acıgöl is a lake in Turkey's inner Aegean Region, in a closed basin at the junction between Denizli Province, Afyonkarahisar Province and Burdur Province. The lake attracts attention due to its sodium sulfate reserves. Turkey's largest commercial sodium sulfate production operations are based here. Mirabilite and tenardite are common sodium sulphate minerals that are produced from this lakes.

Sodium sulphate from salty or bitter alkali lakes can be produced in natural and artificial methods. This decision is differs by the facilities production area and capacity. Solution mining method of sodium sulphate is examined in detail. Also, room and pillar method is examined briefly.

By comparing these methods, solution mining step forwards with its advantages. But in salt lakes, where the lake area is wide and weather temperature conditions are optimum for the operation method or where by changing of the seasons last product can be collected by freezers from the lakes surface. Therefore any facility for the production is needed and so in this case solution mining method isn't advantageous.