Modern sedimentation rate and heavy metal accumulation in Jiaozhou Bay sediments

J. QI

Guangdong Food and Drug Vocational College, Guangzhou 510520, PR China (jungzh@163.com)

Introduction

The sediments that accumulate in Jiaozhou Bay of the Shandong Peninsula recorded the information about the history of changes in the source of the material, the rate of deposition and the influence of human activies [1, 2]. Six cores were collected from the Jiaozhou Bay by the Cruise work on Gold Star boat on Sep. 6th, 2003. The ^{210}Pb radioactivities of the sediments were determined by ^{210}Pb geochronology method and ICP-MS was employed for the determination of Zn, Cu, Cr, Ni, Pb, Cd and Co concentrations.

Discussion of Results

The sedimentation rates were found to be higher in margin areas of the bay, especially in the dumping areas, where the rates were about 0.77cm/a ~ 3.96cm/a. While in the central region of the bay, there was a patch of fine-grained mud, with the sedimentation rates being lower. The profiles ^{210}Pb radioactivity at sample cores mostly appeared in two-segment model, which indicate that the modern sedimentary environment of this region was very stable. Differences in the profiles reflect spatial and temporal variations in hydrodynamic conditions and the grain size of sediments in the Jiaozhou Bay.

The main heavy metals in the sediments of Jiaozhou Bay were Zn, Cu, Cr, Ni and Pb, while the concentrations of the elements Cd and Co were much lower. The concentrations of the main heavy metals of the sediments in Jiaozhou Bay were higher than that in the China Shelf Sea, which showed that the area had been contaminated to a certain extent. But these concentrations were low in comparison with the highest background level in former global modern industrialization times and that in other industrialized areas. The heavy metal profiles Zn, Cr, Ni, Co and Pb from the six cores showed a high variability, but also a decreasing trend since 1980s, while the element Cu presented an increasing trend and the element Cd presented a more chaotic profile than the other elements.

[1] Stanley *et al*. (2000) *Geology* **28**, 259–298. [2] Ruiz-Fermandez *et al*. (2004) *J Environ Radioactiv* **76**, 161–175.

The bioavailability of selenium and risk assessment for human selenium poisoning in Se-high areas, China

H-B. QIN[1,2], J-M. ZHU[1]* AND H. SU[3]

[1]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China (*correspondence: zhujianming@vip.gyig.ac.cn)

[2]Graduate University of Chinese Academy of Sciences, Beijing 100049, China

[3]Center for Disease Control and Prevention of Enshi Prefecture, Enshi 445000, China

Enshi, China, is one of the selenosis areas in the world, where sporadic cases of selenium (Se) poisoning in livestock and human were still being found at present. However, selenium bioavailibility in soils and current situation on intake of Se by human have not been reported in detail. In this study, selenium levels and its speciation in water and cropland soils, Se content in crops from Enshi were investigated, as well as estimating the daily intake of Se by local residents. Results showed that the geometric mean of Se concentration was 54.2 μg/L (2.0-519.3 μg/L, *n*=62) and 6.2 mg/kg (2.67-87.3 mg/kg, *n*=37) in water and soils, respectively. Selenium content ranged from 0.18 mg/kg to 37.1 mg/kg in crops, which was dependent on crop species and Se bioavailability in soils. On the basis of consumption and Se contents of foods, cereal consumption is the major pathway of Se intake by local residents, followed by vegetables, meats, and drinking water. The total daily intake of Se was approximately 3000 μg/day for human in Se-high areas in Enshi, which was considerably higher than the upper tolerable nutrient levels (UL, 400 μg/day) referred by WHO and US EPA, suggesting that a high risk for human chronic Se poisoning still exists in this areas. Furthermore, the daily Se intake through drinking water (108.4 μg/day) was up to 27.1% of referred Se UL. Thus, unlike previous studies, it is should not ignore the contribution of Se in drinking water when assessing the health risk for human daily intake of Se in Se-high areas. Local residents should be advised to avoid planting crops in areas with Se-high soils or irrigated by Se-high water, and to consume foods mixed with the exotic.

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Cr isotope fractionation during biogeochemical reduction of Cr(VI) by Hanford native aquifer microbial communities

L. QIN*, J.N. CHRISTENSEN, S.T. BROWN, L. YANG, M.E. CONRAD, E. SONNENTHAL AND H.R. BELLER

Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720 (*correspondence: lqin@lbl.gov)

Hexavalent Cr contamination in groundwater within the DOE complex has been a long-standing issue. Injection of electron donors, such as lactate, to Cr contaminated aquifers to stimulate the growth of native microbial communities, and thus promote reduction of Cr (VI) to Cr (III), has become a widely utilized remediation practice. However, whether these conditions are optimal for Cr reduction is to a large extent unknown. It has been demontrated that reduction of Cr (VI) can cause Cr isotope fractionation [1, 2]. The Cr fractionation factor changes under varying experimental conditions even with the same bacterial strain [2]. Cr isotopic measurements are more direct and effective than concentration analyses to distinguish between different reduction pathways, and also between reduction and simple dilution.

To evaluate the effects of differing electron acceptors on Cr (VI) reduction by native microbes, small-scale column experiments with homogenized material from the Hanford 100H aquifer were conducted. All columns had a continuous inflow of solutions with constant concentrations of Cr (VI), lactate, and the targeted electron acceptor (nitrate, sulfate, no electron acceptor added). Different Cr fractionation behaviors were observed under different conditions. The least extensive Cr reduction occurred in no-electron-acceptor-added columns and had the largest Cr isotope fractionation (α~0.997). The greatest Cr reduction occurred in two sulfate-containing columns that were fermenting the lactate. Samples from one such column had the smallest Cr fractionation (α~0.999). Denitrifying columns had intermediate α values. One sulfate-added (not fermentative) column showed two distinctive stages of fractionation, suggesting a change in reduction processes. Our α values mostly fall in the range 0.997-0.999, which are smaller than those observed in cell suspension experiments with *Shewanella oneidensis* and much lower lactate concentrations [2]. Reactive tranport modeling will be conducted to further evaluate the effects of various experimental parameters on Cr isotope fractionation.

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[2] Sikora, Johnson & Bullen (2008) *Geochim. Cosmochim. Acta* **72**, 3631–3641.

Precise $^{40}Ar/^{39}Ar$ geochronology of gas migration and accumulation

H.N. QIU[1], J.B. YUN[1,2], H.Y. WU[2] AND Z.H. FENG[2]

[1]State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, CAS, Guangzhou 510640
[2]Exploration and Development Research Institute, Daqing Oilfield Company Ltd., Daqing 163712, China

It is very difficult to determine the exact age of natural gas emplacement because no suitable mineral for dating with common isotope geochronometers was formed during gas migration and accumulation, although illite K-Ar dating has been widely used to constrain the maximum ages of petroleum accumulation since Lee *et al*.'s [1] report. Selby *et al*. [4] demonstrated a possibility to date hydrocarbon deposits by Re-Os isotopes. Mark *et al*. [2] obtained oil migration age by UV laser microprobe $^{40}Ar/^{39}Ar$ dating of authigenic K-feldspar bearing oil fluid inclusions.

In this study, we show a novel promising approach to obtain high precision ages of gas emplacement into the Songliao Basin, NE China, by $^{40}Ar/^{39}Ar$ progressive crushing technique. The igneous quartz from the Cretaceous volcanic rocks in Yingcheng Formation (117–111 Ma) hosting the gas reservoir contains abundant K-rich secondary fluid inclusions (8.3–0.4 wt% in salinity) with high partial pressures of methane (66–9 MPa) trapped during gas emplacement. Based on our previous studies, quartz with abundant K-rich fluid inclusions provides an excellent closed system well suited for $^{40}Ar/^{39}Ar$ progressive crushing technique. Three irradiated igneous quartz samples were measured by stepwise crushing to release these secondary fluid inclusions. All three samples yielded well-defined $^{40}Ar/^{39}Ar$ isochrons with ages in close agreement, precisely constraining that the gas emplacement occurred at 42.4 ± 0.5 Ma (2SD) below the famous Daqing Oil Field in the Songliao Basin, extending possible gas reservoirs from the upper Cretaceous to the middle Eocene.

This study provides a new effective solution to gain the ages of gas emplacement. See [3] for detail.

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The relationship between gabbros and I-type granites in the southeast coast of Fujian, South China: Evidence from *in situ* zircon U-Pb dating, Hf isotopes and whole-rock geochemistry

JIAN-SHENG QIU* AND ZHEN LI

State Key Lab for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China (*correspondence: jsqiu@nju.edu.cn)

Two representative gabbro–granite complexes from Quanzhou (QZ) and Huacuo (HC) in the southeast coast of Fujian, South China have been selected for a detailed geochronological and geochemical study, aiming to probe the genetic relations between the acid and basic magmas.

These complexes are composed predominantly of I-type granitoids, with lesser amounts of hornblende gabbro (<5% of the total igneous rocks). Zircon U-Pb dating yields consistent crystallisation ages of 109 ± 1 and 108 ± 1 Ma for the QZ gabbros and granites, and an age of 111 ± 1 Ma for the HC gabbros, which is contemporaneous with the spatially coexisted HC granites. Both the gabbros and granitoids are enriched in light rare earth elements and large ion lithophile elements (e.g. Rb, Ba, Th and U), and depleted in high field strength elements (e.g. Nb and Ta). Moreover, they show similarly homogeneous Sr–Nd isotopic compositions. All these factors indicate that they are genetically related.

Although the Sr–Nd isotopic signatures of the QZ and HC gabbros seemingly point to an enriched mantle source (EM-1), they have highly variable zircon Hf isotopic compositions, with ε_{Hf} (*t*) values ranging from negative to positive (specifically –4.6 to +6.1 for the QZ gabbros and –4.8 to +11.6 for the HC gabbros). On the other hand, their associated granitoids show relatively high whole-rock $\varepsilon_{Nd}(t)$ values (–2.5 and –4.1 for the QZ and HC granites, respectively), and homogeneous and neutral zircon $\varepsilon_{Hf}(t)$ values (–1.9 to +1.8 for the QZ granite). Based on an integration of petrography, geochronology and geochemistry, we interpret the parental basic magmas of these gabbros have originated from a depleted mantle source, but experienced a significant crustal contamination by the felsic melts that gave rise to the associated granitoids. Contributions from such a depleted mantle source resulted in the growth of juvenile basaltic lower crust, the partial melting of which generated the parental felsic magmas of the QZ and HC complexes.

A new recognition of Grenvillian volcanic suite in the South China Block and its connection with Rodinia assembly

X.F. QIU[1], W.L. LING[1]* AND X.M. LIU[2]

[1]State Key Laboratory of Geological Processes and Mineral Resources, China Univ. of Geosciences, Wuhan 430074, China (qxf_424@yahoo.com.cn,) (*correspondence: wlling@cug.edu.cn)

[2]State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, China (xiaomingliu@263.com)

Contrasting proposals have been suggested for the position of the South China Block (SCB) in the Rodinia reconstruction, which is partly due to a poor understanding of the SCB history during the late Mesoproterozoic to early Neoproterozoic. Here we report a newly recognized Grenvillian arc-volcanic sequence in the Shennongjia area, western SCB. It comprises alkali-, calc-alkaline basalts and tholeiitic andesitic rocks, and is dated at 1152±24 Ma. The alkali basalts have high TiO2, low Mg# (42-55) and positive εNd, and display OIB-like elemental patterns. By contrast, the calc-alkaline basalts have higher Mg# (57-68), Cr and Ni contents and large negative εNd, and exhibit pronounced depletion in HFSE. The andesites show Eu deficiency, HFSE depletion and small negative εNd.

The alkali-, calc-alkaline basalts are suggested to have been derived from depleted asthenospheric- and metasomatised lithospheric mantle sources, respectively, whereas the andesites from mafic lower crustal anatexis; the volcanic sequence was developed within an island-arc setting. Integrating with previously documented works, the western Yangtze craton is suggested to have comprised a collage of microcontinents during the Grenvillian period and underwent a westward lateral continental growth by subduction accretion and subduction-related collision. Increasing lines of evidence infer a western Yangtze-South Australia connection during Rodinia assembly, which provides a new insight into the SCB position in the supercontinent.

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Raman spectroscopic analysis of heterogeneous carbonaceous matter in the 2.0 Ga Zaonega Fm, Karelia, Russia

Y. QU[1]*, M.A. VAN ZUILEN[1,2] AND A. LEPLAND[3]

[1]Centre for Geobiology, University of Bergen, Allegaten 41, 5007, Bergen, Norway (*correspondence: Yuangao.Qu@geo.uib.no)

[2]Equipe Geobiosphere, Institut de Physique du Globe - Sorbonne Paris Cité, Université Paris Diderot, CNRS, 1 rue Jussieu, 75238 Paris cedex 5, France (vanzuilen@ipgp.fr)

[3]Geological Survey of Norway, Leiv Eirikssons vei 39, 7491 Trondheim, Norway (Aivo.Lepland@NGU.NO)

Carbonaceous matter in sediments is gradually matured during metamorphism, as increased temperature causes structurally disordered organic molecules to rearrange themselves progressively into crystalline graphite. Raman spectroscopy is commonly used to describe the degree of this transformation, since the relative band intensities at 1350 cm-1 (D1) and at 1580 cm-1 (G) can be directly related to the defect-bound crystal domain size of graphitic crystallites. Intensity-based (R1) and especially area-based (R2) band ratios of carbonaceous matter have therefore been used as reliable indicators for the metamorphic grade that a rock has experienced.

The 2.0 Ga old Zaonega Formation in Karelia, Russia, contains sediments that are highly enriched in organic carbon. They represent the first known record of oil generation and migration on Earth, and form a key target for drill-core-based studies on the evolution of life during the Archean-Paleoproterozoic transition period. Carbonaceous matter consisting of residual kerogen and pyrobitumen throughout the succession has experienced local contact-metamorphism caused by gabbroic sills and lava flows, regional greenschist-facies metamorphism, and migration in silicate saturated fluid systems. This complex geologic history prevents simple straightforward interpretation of original isotopic ($\delta^{13}C$) and chemical characteristics of carbonaceous matter, and requires an *in situ* tool such as Raman spectroscopy to distinguish between variously altered carbonaceous fractions and small scale heterogeneities.

Here we report the variation in Raman spectral indicators R1 and R2 of carbonaceous matter throughout a 7 m long drill-core section that represents the upper contact zone of a gabbroic sill. Considerable heterogeneity in both R1 and R2 on a small spatial scale, indicates that factors other than temperature - such as organic precursor material, mineral matrix, and local variation in stress and strain - have influenced the overall process of graphitization. The implications for Raman-based geothermometry on complex metamorphic terrains will be discussed.

Estimating aerosol forcings using the MACC aerosol reanalysis

JOHANNES QUAAS[1]* AND NICOLAS BELLOUIN[2]

[1]Institute for Meteorology, University of Leipzig, Stephanstr. 3, D-04103 Leipzig, Germany (*correspondence: johannes.quaas@uni-leipzig.de)

[2]Hadley Centre, Met Office, FitzRoy Road, Exeter EX1 3PB, United Kingdom (nicolas.bellouin@metoffice.gov.uk)

In the EU-funded project 'Monitoring Atmospheric Composition and Climate' (MACC), MODIS satellite retrievals of aerosol optical depth (AOD) are assimilated into the IFS global atmospheric model enhanced by an aerosol module, and used for quasi-operational numerical weather forecasts. This MACC aerosol reanalysis yields a 3D field of concentrations of different aerosol components consistent with the MODIS AOD retrievals, along with the reanalysis of meteorological fields, and cloud and radiation distributions as computed by the model. This new dataset provides a unique opportunity to estimate aerosol climate forcings. On the basis of the method by Bellouin *et al*. [1] and Quaas *et al*. [2], where the aerosol radiative forcings have been derived from satellite data, we develop an improved method using this new dataset. Preliminary results show a global annual (year 2003) mean radiative forcing by the aerosol direct effect of -0.5 Wm^{-2}, and an indirect effect (first indirect effect or Twomey effect) of -0.3 Wm^{-2}. The product now also allows for a detailed analysis of the spatial and temporal variability of aerosol forcings.

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Diamond-facies fluid flow during subduction: Evidence & consequence

ALEX QUAS-COHEN[1]*, SIMON CUTHBERT[2], GILES DROOP[1], CHRIS J. BALLENTINE[1] AND RAY BURGESS[1]

[1]School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, UK (*correspondence: alexandra.quas-cohen@postgrad.manchester.ac.uk)
[2]School of Sciences, University of the West of Scotland, Paisley, UK (Simon.Cuthbert@uws.ac.uk)

Exhumed, subducted crustal terranes record the most extreme metamorphic conditions that continental rocks are known to experience and enable us to gain insight into the more elusive systems and processes of the Earth. Abundant fluid flow and fluid-rock interaction is evident during subduction even at the highest-grade conditions: numerous veins within a Fe-Ti, crustal garnet peridotite body in the Western Gneiss Region (WGR) of Norway contain microdiamonds [1]. Many questions remain unanswered regarding fluids and interactions at these depths. Our study focuses on the metasomatism of ultra-high pressure (UHP) rocks in the WGR; in particular, on determining the signature, source and recycling of noble gases and halogens. I present field maps and sketches of various UHP WGR localities to demonstrate the petrophysical relationships between various rock-types and features which demonstrate the nature and composition of intruding fluids; particularly, the associations of pegmatitic garnet websterites, carbonaceous and hydrous phases and different vein-types with Fe-Ti garnet peridotite and bimineralic eclogite bodies. I also present preliminary geochemical data demonstrating phase compositions, P-T conditions, chemical change due to fluid-rock interaction and noble gas compositions. Data gathered so far indicates that garnet websterites represent metasomatised domains of the peridotite and eclogite bodies within the WGR.

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The impact of transported pollution on Arctic climate

P.K. QUINN[1] *, A.S. STOHL[2], A. ARNETH[3], T. BERNTSEN[4], J. BURKHART[2], M. FLANNER[5], K. KUPIAINEN[6], M. SHEPHERD[7], V. SHEVCHENKO[8], H. SKOV[9] AND V. VESTRENG[10]

[1]NOAA PMEL, Seattle, WA, USA (*correspondence: patrcia.k.quinn@noaa.gov)
[2]Norwegian Institute for Air Research, Kjeller, Norway (ast@nilu.no, jfb@nilu.no)
[3]Lund University, Lund, Sweden (Almut.Arneth@nateko.lu.se)
[4]University of Oslo, Oslo, Norway (t.k.berntsen@geo.uio.no)
[5]University of Michigan, Ann Arbor, MI , USA (flanner@umich.edu)
[6]Finnish Environment Institute, Helsinki, Finland (Kaarle.Kupiainen@ymparisto.fi)
[7]Environment Canada, Toronto, Canada (marjorie.Shepherd@ec.gc.ca)
[8]P.P. Shirshov Institute of Oceanology of the Russian Academy of Sciences, Moscow, Russia (vshevch@ocean.ru)
[9]Aarhus University, Roskilde, Denmark (hsk@dmu.dk)
[10]Norwegian Pollution Control Authorities, Oslo, Norway (Vigdis.Vestreng@klif.no)

Arctic temperatures have increased at almost twice the global average rate over the past 100 years [1]. Warming in the Arctic has been accompanied by an earlier onset of spring melt, a lengthening of the melt season, changes in the mass balance of the Greenland ice sheet, and a decrease in sea ice extent. Short-lived, climate warming pollutants such as black carbon (BC) have recently gained attention as a target for immediate mitigation of Arctic warming in addition to reductions in long lived greenhouse gases. Model calculations indicate that BC increases surface temperatures within the Arctic primarily through deposition on snow and ice surfaces with a resulting decrease in surface albedo and increase in absorbed solar radiation. In 2009, the Arctic Monitoring and Assessment Program (AMAP) established an Expert Group on BC with the goal of identifying source regions and energy sectors that have the largest impact on Arctic climate. Here we present the results of this work and investigate links between mid-latitude pollutants and Arctic climate.

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Pressure induced phase transitions in $MnTiO_3$: Insights from first principles

CARMEN QUIROGA* AND ROSSITZA PENTCHEVA

Section Crystallography, Department of Earth and Environmental Sciences, Ludwig-Maximilians Universität München
(*correspondence:
Carmen.Quiroga@lrz.uni-muenchen.de,
Pentcheva@lrz.uni-muenchen.de)

$MnTiO_3$ is an example of an ABO_3 compound which at ambient conditions crystallizes in the ilmenite structure and remains stable at least up to 26 GPa [1]. A denser $LiNbO_3$ phase can be quenched from high pressure and high temperature experiments to ambient conditions [2].

Using density functional theory calculations we determine the ground state properties and magnetic coupling of $MnTiO_3$ in the ilmenite, perovskite, $LiNbO_3$ and postperovskite phases. As $MnTiO_3$ is a strongly correlated material, we explore the influence of the exchange correlation functional beyond the local density and the generalized gradient approximations within LDA/GGA+*U* method and hybrid functionals. Our calculations show that ilmenite is the most stable phase at ambient conditions. The $LiNbO_3$ transforms into the perovskite phase at ~2.5 GPa in agreement with experiments [3]. A transition from perovskite to the post-perovskite phase ($CaIrO_3$-type) is predicted at pressures above 50 GPa.

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