



Frontiers Meeting 2012

Nanogeoscience:
A New Frontier in Science and Technology
for Earth and Environment Systems

10 December 2012

PROGRAMME

09.45	Registration & coffee
10.15	Introduction
10.20	'Why Nanogeoscience?' David Vaughan, <i>University of Manchester</i>
10.45	The Biogeochemistry of Coal Mine Drainage: Microbes, Green Rust and the Factors Controlling Iron Mineralogy in Coal Mine Drainage Nia Blackwell, <i>Institute of Geography and Earth Sciences, Aberystwyth</i>
11.05	Tea & coffee
11.25	Characterisation of Nanoparticles and Associated Metals in Landfill Leachates Yasmin Labibi, <i>University of Southampton</i>
11.45	Maturation and Ageing in Biominerals with Application to Enamel Maturation Anastasios Papadimitriou, <i>University of Birmingham</i>
12.05	Reactivity and Toxicity of Engineered Nanoparticles Éva Valsami-Jones, <i>University of Birmingham</i>
12.35	Lunch (provided for all delegates)
13.35	Bioavailability and Persistence of Three Isotopically Labelled Forms of ⁶⁸ Zn in the Estuarine Snail, <i>Peringia Ulvae</i> Adam Laycock, <i>Imperial College London</i>
13.55	Modelling the Structure, Transport and Reactivity of Metallic Nanoparticles – Towards Modelling Nanotoxicity of Silver Nanoparticles Paul Martin, <i>University of Birmingham</i>
14.15	Tracing Bioavailability of ZnO Nanoparticles Using Stable Isotope Labeling Fiona Larner, <i>Imperial College, London</i>
14.35	Characterisation and Applications of Bio-geo-nanoparticles Victoria Coker, <i>University of Manchester</i>
15.05	Nanoparticle Bioremediation Rebecca Skuce, <i>University of Glasgow</i>
15.25	Tea & coffee
15.45	Biogenic Reactive Nanominerals for the Remediation of Contaminated Soils and Waters Mathew Watts, <i>Williamson Research Centre, University of Manchester</i>
16.05	Iron-Rich Nanoparticle Formation and Importance for Trace Metal Transport in Ground Water and Arctic Rivers Björn Stolpe, <i>University of Birmingham</i>
16.25	Discussion
17.00	Close of day and drinks reception

Oral Presentation Abstracts (in presentation order)

Why Nanogeoscience?

David J. Vaughan

Williamson Research Centre for Molecular Environmental Science, and School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL (UK)

Over recent decades, there have been dramatic developments in techniques for studying nanometre sized particulate materials that occur naturally, or that can be synthesised in the laboratory or on an industrial scale. Nanomaterials commonly have properties which are distinct from their larger sized compositional equivalents (for example, the solubility of quartz increases by several orders of magnitude when entering the nanometre size range).

Nano-particles play a key role in the geochemical cycling of the chemical elements in the so-called 'critical zone' at Earth's surface, not least because they have relatively large surface areas for the uptake of toxic materials ranging from radioactive species to organic pollutants and inorganic pollutants such as arsenic. The fabrication of engineered nanoparticles (nanotechnology) for applications ranging from medicine to advanced materials is now a multi-million pound industry. Consequently, another aspect of nanogeoscience research concerns the investigation of the fate of engineered nanoparticles released into the environment and their potential impact on ecosystems and, ultimately, on human health. Research on engineered nanoparticles, particularly synthetic biominerals produced using methods involving bacteria, is also directed towards the fabrication of new materials for application in areas ranging from catalysis to environmental clean-up.

Some examples of interactions involving nanoparticles in acid minewaters, modern sediments and the atmosphere, and studied using advanced imaging and analytical techniques, will be briefly discussed along with other developments at the interface between nanotechnology and the geosciences.

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The Biogeochemistry of Coal Mine Drainage: Microbes, Green Rust and the Factors Controlling Iron Mineralogy in Coal Mine Drainage

N. Blackwell¹, W. Perkins², G. Griffith², J. Bearcock³, B. Palumbo-Roe³, B. Johnson⁴, K. Hallberg⁴, A. Edwards²

¹*Institute of Geography and Earth Sciences, Aberystwyth, Wales, UK*

²*Institute of Biological, Environmental and Rural Sciences, Aberystwyth, Wales, UK*

³*British Geological Survey, Keyworth, Nottingham, UK*

⁴*School of Biological Sciences, Bangor, Wales, UK*

Green rust (GR), an iron-bearing mineral, has been shown in studies to reduce and even remove harmful contaminants from water and has the potential to play a key role in both passive and active treatment remediation systems.

GR can be synthesised in the laboratory using man-made chemicals although producing the amount required for use in remediation systems in this way may not be the most cost effective process. It has been found in the natural environment, for example, at a site in South Wales where mineralogical transformations within accumulations of ochreous coal mine drainage sediment have occurred in the anoxic environments beneath the surface.

Aberystwyth University, in collaboration with Bangor University and the British Geological Survey, is currently investigating the unique geochemical and microbial parameters at the South Wales site. Once these parameters are fully understood the aim is to recreate these natural conditions which form GR in the laboratory and, by adding ochreous mine waste sediment to the system, produce GR. Preliminary studies have identified *Geothrix sp.* and *Rhodoferax sp.* within the ochre which precipitates from the circum neutral, iron- and sulphate-rich waters at the site (80 and 900 mg L⁻¹, respectively). Both genera contain iron reducing species and current studies are focusing on promoting iron reduction within the ochre using a variety of organic substrates as electron donors. If the project is successful, GR can then be created sustainably in sufficient quantities to be applied in remediation systems using widely available ochreous sediment and naturally occurring microbes.

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Characterisation of Nanoparticles and Associated Metals in Landfill Leachates**Yasmin Labibi***University of Southampton*

Landfill leachates contain a wide range of pollutants such as potentially toxic metals (e.g. chromium, arsenic and cadmium). Current models of landfill lining systems predict the fate and transport of these pollutants in the environment, however at present these models do not consider the presence and effect of nanoparticles (NPs). NPs from landfill leachates must therefore be studied in order to gain knowledge and understanding of their chemical, structural and behavioural characteristics with respect to their interactions with potential pollutants, particularly where these influence transport within landfill liners. This information is fundamental for the development of more robust pollution risk assessment models. This study examines landfill leachates from UK municipal solid waste sites, which have been characterised using multiple techniques (asymmetric flow field-flow fractionation with UV-Vis and fluorescence detection, dynamic light scattering, atomic force microscopy, and high resolution inductively coupled mass spectrometry) in order to determine characteristics such as NP size distribution, shape and particle inorganic and organic chemical influences upon associated metal distributions. Preliminary results show that two distinct size fractions are present in leachates with most metals associated with low molecular weight organic NPs.

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Maturation & Ageing in Biominerals with Application to Enamel Maturation**A. Papadimitis¹, R. Lynch², E. Valsami – Jones¹**¹*University of Birmingham, Department of Geography, Earth & Environmental Sciences, Edgbaston, Birmingham, B15 2TT, UK*²*GlaxoSmithKline, R&D Customer Healthcare, Weybridge, Surrey, KT13 0DE, UK*

Enamel formation and maturation is a progressive and complex process divided into three stages. The first stage, called the secretory stage, involves the formation of partially mineralized enamel through proteins and an organic matrix. The second stage is the pre-eruptive maturation of the formed enamel and the third and final stage is the post-eruptive maturation, when the mineralization process is completed after tooth eruption and exposure to oral fluids. [1,2] So far, most studies have focused either on biological [3] or chemical [4] alterations without taking into account the dissolution/ re-precipitation mechanisms or the role of fluoride (and potentially other species) uptake, which may result in increased enamel (biological apatite) stability and hardness. [5] The physical and chemical changes happening on the enamel's surface are of great importance. Monitoring these alterations would allow the development of a model that describes the process of post-eruptive maturation and the synthesis of appropriate apatite proxies. However, due to the nanoscale nature of these changes this is difficult to accomplish. The vast development, though, of measuring and characterization techniques for nanosized particles facilitates these observations.

The primary aim of this project is to study the kinetics of simulated enamel transformation in the oral environment and to monitor changes in enamel solubility due to ageing. For this purpose enamel taken from human and bovine teeth will be tested, using the appropriate demineralization/remineralization as well as characterization techniques. The results will be then applied for the synthesis of isotopically and chemically doped apatite proxies and to evaluate whether these proxies can be used as enamel substitutes in dental research.

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Reactivity and Toxicity of Engineered Nanomaterials

Eugenia Valsami-Jones

School of Geography Earth & Environmental Sciences (GEES), University of Birmingham, Edgbaston, Birmingham, B15 2TT (UK)

Over recent decades, there have been dramatic developments in nanoscale technological applications. Many of these developments involve the creation of nanomaterials, nanoscale objects designed to have unique properties. We still do not fully understand the range of properties of nanomaterials, or the full technological potential of their novel structures. It is, however, possible that along with novel physicochemical properties nanomaterials may also develop toxicity in unexpected ways.

I will be presenting an overview of recent research towards a better understanding of reactivity at the nanoscale and potential links to toxicity, particularly focusing on the environmental fate and behaviour of nanomaterials.

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Bioavailability and Persistence of Three Isotopically Labelled Forms of ⁶⁸Zn in the Estuarine Snail, *Peringia Ulvae*

Adam Laycock¹, Farhan Khan², Agnieszka Dybowska², Fiona Lerner¹, Eva Valsami-Jones^{2,3}, Mark Rehkämper¹

¹Dept of Earth Science & Engineering, Imperial College, London, SW7 2AZ, U.K.

²Natural History Museum, London, SW7 5BD U.K.

³University of Birmingham, Birmingham, B15 2TT, U.K.

The bioavailability and persistence of ZnO nanoparticles, micron size ZnO particles and dissolved Zn in the estuarine snail, *Peringia ulvae*, were determined following waterborne exposures at environmentally relevant exposure concentrations of 20 µg/l. Stable isotope labelling was employed to trace the transport of Zn, whereby each form was produced from Zn-68 that was isotopically enriched to >99%, compared to a natural abundance of 18.8%. Zn isotope analyses of water and tissue samples were carried out at high precision (better than ±0.05%, 2RSD) by MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometry).

The concentration of Zn in a sample from the isotopically labelled source can be calculated from the measured differences in Zn isotope compositions. An increase in the overall Zn concentration of only 0.08‰ by the presence of a Zn-68 enriched source already creates an observable deviation in the isotope composition, when analysed by MC-ICP-MS. This provides a detection sensitivity that is by far superior to conventional methods of analysis, where total Zn concentration measurements are used. This is one of the first studies to employ stable isotope labelling in conjunction with high-precision mass spectrometry, to accurately quantify the transport and fate of manufactured nanomaterials at realistic concentrations and conditions.

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Modelling the Structure, Transport and Reactivity of Metallic Nanoparticles – Towards Modelling Nanotoxicity of Silver Nanoparticles

Paul Martin

School of Geography, Earth and Environmental Sciences, University of Birmingham

There is growing interest in understanding the relationship between the physical and chemical properties of nanomaterials and their potential risk to the environment and human health.

As the technological benefits of nanotechnology begin to rapidly move from laboratory to large-scale industrial application, release of nanomaterials to the environment including water, soil, sediment, and biosolids is inevitable. Concerns have been raised that the special properties of nanostructured materials that make them so attractive could potentially lead to unforeseen health risk or environmental hazards.

Silver nanoparticles (Ag-NPs) are finding wide usage including areas of catalysis, optical sensors, electronics, and as an anti-bacterial agent. There are health concerns however, but key parameters affecting biological activity have not been fully elucidated. The characterisation of Ag-NPs physico-chemical properties is therefore essential for assessing their potential for toxicity.

We describe how our atomistic simulations are helping to make predictions of Ag-NP size distribution, morphological features like shape, surface area and solvent accessibility; stability; thermodynamics; solubility and dissolution; state of dispersion; defect and surface chemistry. We further consider how these nano-properties might affect their transport, activity and toxicity in geological and biological contexts.

We conclude by illustrating the potential of our computer models for interdisciplinary work and how they are becoming useful synergistic tools for scientific investigations of Ag-NP properties and potential nanotoxicity.

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Tracing Bioavailability of ZnO Nanoparticles Using Stable Isotope Labeling

Fiona Lerner¹, Yuktee Dogra², Agnieszka Dybowska³, Julia Fabrega², Björn Stolpe⁴, Luke J. Bridgestock¹, Rhys Goodhead⁵, Dominik J. Weiss^{1,3}, Julian Moger⁵, Jamie R. Lead⁴, Eugenia Valsami-Jones³, Charles R. Tyler², Tamara S. Galloway², Mark Rehkämper^{1,3}

¹Department of Earth Science & Engineering, Imperial College London, SW7 2AZ, UK

²Biosciences, College of Life and Environmental Sciences, The Geoffrey Pope Building, University of Exeter, EX4 4QL, UK

³Department of Mineralogy, Natural History Museum, London, SW7 5BD, UK

⁴School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

⁵School of Physics, University of Exeter, EX4 4QL, UK

Zinc oxide nanoparticles (ZnO NPs) are widely used in commercial products and knowledge of their environmental fate is a priority for ecological protection. Here we synthesized ZnO NPs that were made from and thus labeled with the stable isotope ⁶⁸Zn and this enables highly sensitive and selective detection of labeled components against high natural Zn background levels. We combine high precision stable isotope measurements and novel bioimaging techniques to characterize parallel water-borne exposures of the common mudshrimp *Corophium volutator* to ⁶⁸ZnO NPs, bulk ⁶⁸ZnO and soluble ⁶⁸ZnCl₂ in the presence of sediment. *C. volutator* is an important component of coastal ecosystems where river-borne NPs will accumulate and used on a routine basis for toxicity assessments. Our results demonstrate that Zn from ZnO NPs is bioavailable to *C. volutator* and that Zn uptake is active. Bioavailability appears to be governed primarily by the dissolved Zn content of the water, whereby Zn uptake occurs via the aqueous phase and/or the ingestion of sediment particles with adsorbed Zn from dissolution of ZnO particles. The high sorption capacity of sediments for Zn thus enhances the potential for trophic transfer of Zn derived from readily soluble ZnO NPs. The uncertainties of our isotopic data are too large, however, to conclusively rule out any additional direct uptake route of ZnO NPs by *C. volutator*.

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Characterisation and Applications of Bio-Geo-Nanoparticles

Victoria S. Coker

Williamson Research Centre for Molecular Environmental Science, and School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL (UK)

Biological processes, particularly microbially-mediated redox reactions, can lead to the formation of a wide range of different nanoparticles, including magnetic and catalytically active materials. This 'green chemistry' route to the formation of novel materials can find applications in the remediation toxic metals, as antimicrobial agents or as quantum dots for electronic and optical devices [1].

An Fe(III)-reducing bacteria, *Geobacter sulfurreducens*, was used to form tailored nano-ferrites through the substitution of Co for Fe within the structure of biogenic magnetite (Fe_3O_4) with enhanced magnetic properties [2]. In addition, this same bacterium can be used to form a nano-Pd catalyst supported on biogenic nanomagnetite for use in fine chemical synthesis reactions [3].

Characterisation of nanoscale materials is a complex process requiring state-of-the-art techniques. A nanoscale imaging technique, scanning transmission X-ray microscopy (STXM), was used to chemically map biogenic magnetite redox states in relation to microbial components within the system. This technique shows that there is a surprising degree of variation on the nanoscale within these complex systems [4]. Understanding these electron transfer processes at the nanoscale is critical for optimising the remediation of toxic metals and radionuclides via these bioengineered Fe nanoparticles.

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Nanoparticle Bioremediation

R.L. Skuce, D. J. Tobler, M. R. Lee, V R. Phoenix

School of Geographical and Earth Sciences, University of Glasgow, Glasgow, G12 8QQ, UK

The use of engineered nanoparticles continues to expand rapidly. As this intensifies, so does the environmental risk posed if they are released into the environment. This is of great concern due to the potential toxicity of some nanoparticles. As it stands, we are poorly prepared to deal with nanoparticle pollution and thus remediation strategies must be developed. Here solid phase capture is used as a means of removing nanoparticles from aquatic systems. In this process, nanoparticles are trapped within minerals as they precipitate and grow. This process has been investigated for the removal of radionuclide and trace element contaminants in groundwater systems¹, however, its potential to immobilise and remediate nanoparticles from polluted waters has yet to be examined.

Preliminary experiments showed that electrostatic interactions between the growing mineral surface and the nanoparticle greatly controlled the degree of nanoparticles capture. As a result, a mineral precipitating system can be specifically tailored to suit the surface character of the nanoparticle under investigation. For example, a calcite precipitating mineral system showed high rates of nanoparticle capture in the case of negatively charged nanoparticles, due to electrostatic attraction between the positive calcite surface and the negative nanoparticle. In contrast, positively charged nanoparticles were poorly incorporated within calcite crystals, and a struvite precipitating mineral system showed much higher success, due the negative surface charge of struvite. Overall, batch experiments showed the successful removal of both negative and positive highly stable organo-metallic nanoparticles at concentrations up to 10 mg/l (the highest concentration tested thus far).

This technology has the potential for application in contaminated groundwaters and soils as an in-situ remediation technique for nanoparticle pollutants.

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Biogenic Reactive Nanominerals for the Remediation of Contaminated Soils and Waters

Mathew P Watts¹, Russell Thomas², Robert Kalin³, Jonathan R. Lloyd¹

¹*School of Earth, Atmospheric and Environmental Sciences and Williamson Research Centre for Molecular Environmental Science;*

²*Environment, Parsons Brinckerhoff;*

³*University of Strathclyde, UK*

Interactions at the microbe-mineral interface are known to produce reactive nano-scale biomineral phases. These biogenic nanominerals are able to induce the transformation of toxic metals to less soluble forms, and also promote the degradation of organic contaminants in the subsurface. These can therefore be harnessed in an innovative “bionanoremediation” approach to contaminated land problems.

The focus of this study was the reactive Fe(II)-bearing mineral phase magnetite biosynthesised by dissimilatory Fe(III) reduction of a starting Fe(III) phase by the subsurface bacterium *Geobacter sulfurreducens*. The reactivity of the biogenic nanomagnetite was enhanced by functionalization of the surface with Pd nanoparticles. Thus forming a magnetically recoverable bio-nanocatalyst, which exhibits sustained reactivity when supplied with a suitable electron donor such as hydrogen. These nanoparticles were then be applied to the “real life” contaminated problem of alkaline Cr(VI) leachates from the South East of Glasgow, UK. Once a centre for chromite ore processing, landfilling of large quantities of cementitious waste material has caused extensive Cr(VI) contamination of ground and surface waters. Both the biogenic nanomagnetite and the Pd functionalised nanomagnetite exhibited a capacity to reduce the mobile, toxic Cr(VI) to a non-toxic and insoluble Cr(III) phase within environmental samples. Ongoing studies have extended this concept to the treatment of recalcitrant, toxic organic contaminants in sediments. Using a variety of analytical techniques these studies have been able to demonstrate the ability of biogenic nanophases for application to contaminated land problems.

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Iron-Rich Nanoparticle Formation and Importance for Trace Metal Transport in Ground Water and Arctic Rivers

Björn Stolpe¹, Dan Lapworth², Jamie Lead³, Laodong Guo⁴, Alan M. Shiller⁵ Daren C. Goody²

¹*School of Geography Earth and Environmental Science, University of Birmingham, UK*

²*British Geological Survey, UK*

³*Nanoenvironmental Research and Risk Assessment, University of South Carolina, USA*

⁴*School of Freshwater Sciences, University of Wisconsin-Milwaukee, USA*

⁵*Department of Marine Science, University of Southern Mississippi, USA*

The occurrence, size distribution, aggregation and trace-metal binding of iron-rich nanoparticles in groundwater and river water have been studied using a range of sophisticated nanoanalytical techniques. Atomic force microscopy (AFM) performed under oxygen free conditions showed that sub-oxic groundwater samples from the River Thames flood plain were dominated by discrete semispherical nanoparticles in the 1 nm-20 nm diameter range. Transmission and scanning electron microscopy (TEM and SEM) with energy dispersive X-ray spectroscopy (EDS) detection confirmed that Fe was the major element in the nanoparticles. The field results were validated by AFM-analysis of laboratory mixes of Fe(II)-sulphate with Suwannee River Humic or Fulvic acid, yielding nanoparticles with a similar size distribution as in the natural groundwaters. Aeration of both natural groundwaters and laboratory mixes resulted in aggregation of the nanoparticles to become colloids, several hundred nm in diameter. Flow Field-Flow Fractionation coupled on-line to Inductively Coupled Plasma Mass Spectrometry (FIFFF-ICP-MS) showed that dissolved rare earth elements (REEs) in rivers of the Yukon River basin, Alaska, during the spring flood were largely (around 40-50 %) associated to <8 nm organic/iron-rich nanoparticles, presumably eroded from the upper organic-rich soil horizons. During summer base flow, with higher groundwater inputs to the rivers, REEs were mostly associated to small (<0.5 nm) complexes, but also bound to 0.5-3 nm fulvic acid and 4-40 nm and >40 nm iron-rich nanoparticles and colloids. Nanoparticle, sources, formation and dynamics in the Alaskan rivers will be discussed by comparison with the results from sub-oxic groundwater samples, and their implications for the trace-metal transport by Arctic rivers will be examined.

NOTES

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Ground Floor Plan of the Geological Society, Burlington House, Piccadilly

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