



GEOANALYSIS

LEOBEN 2015

**THE 9TH
INTERNATIONAL
CONFERENCE**

ON THE ANALYSIS
OF GEOLOGICAL AND
ENVIRONMENTAL
MATERIALS

**9-14
AUGUST
2015**

**MONTANUNIVERSITÄT
LEOBEN - AUSTRIA**





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Dear Delegate,

Welcome to the 9th International Conference on the Analysis of Geological and Environmental Materials, Geoanalysis 2015. The organising committee, the staff of the Montanuniversität and the City of Leoben are honoured and delighted to host and meet you here in the heart of Upper Styria, Austria and Europe!

The Montanuniversität Leoben was selected by the IAG Council because of the importance of the Montanuniversität as a leading technical university in the education of mining and petroleum engineers and as a thriving hotspot for research in material, polymer, metallurgical and applied earth sciences. The Montanuniversität is proud to celebrate its 175th anniversary in 2015. In the nineteenth century engineers had been sent out to transfer knowledge from the leading British industry to the undeveloped mining districts of Styria. This initiative of Archduke Johann was the foundation of our university as the prime research centre for mining and metallurgy in Central Europe. It is the triannual Geoanalysis conference series that brings together scientists from all continents to share their knowledge for the advancement of science in geoanalysis – the science of analytical chemistry applied to geological and environmental samples – here in Leoben. As such this meeting really crosses as issues related to geoanalysis are not confined within one nation's boundaries.

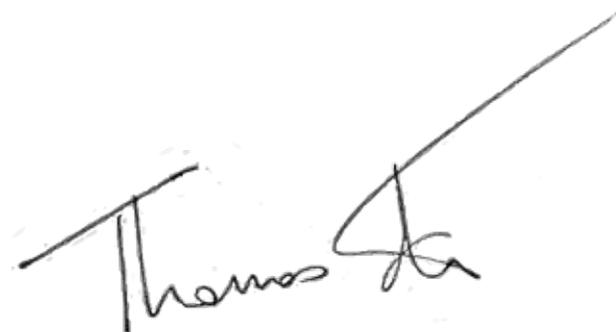
Specialists are needed to understand the characteristics of the studied material to apply the appropriate sampling strategy, sample preparation and instrumentation that is fit-for-the-purpose. This understanding is needed not only from an academic but also from an economic standpoint. A geoanalyst is not just interested in obtaining true values for the measurand with the lowest possible associated measurement uncertainty but also to achieve cost effectiveness. Geoanalysts are able to communicate with the field geologist and the analytical chemist

and more and more are confronted with accreditation bodies as the certification of testing laboratories is taking place throughout governmental and academic institutions. The IAG has a longstanding tradition in providing and organising the well-established laboratory proficiency testing programme GeoPT™.

Certification of reference materials is another core business of the IAG. Through the production and certification of geological reference materials the IAG serves the global community. Matrix-matched certified reference materials are needed not only for traditional bulk rock and environmental sample analysis but also in the thriving field of microanalytical methods, in particular laser ablation ICP-MS. Special short courses and scientific sessions devoted to GeoPT™, reference materials, laser ablation ICP-MS and microanalytical techniques in general highlight the importance of these areas within geoanalysis.

This conference was made possible by the generous support of many companies building excellent analytical instruments that geoanalysts use.

I hope you will be able to enjoy the breadth of exciting applications within geoanalysis presented by scientists from all over the world happy to share and to learn during the Geoanalysis 2015 conference. Please take home new impressions and memories from your wonderful colleagues you met here in beautiful Leoben, Styria.



President of the International Association of Geoanalysts



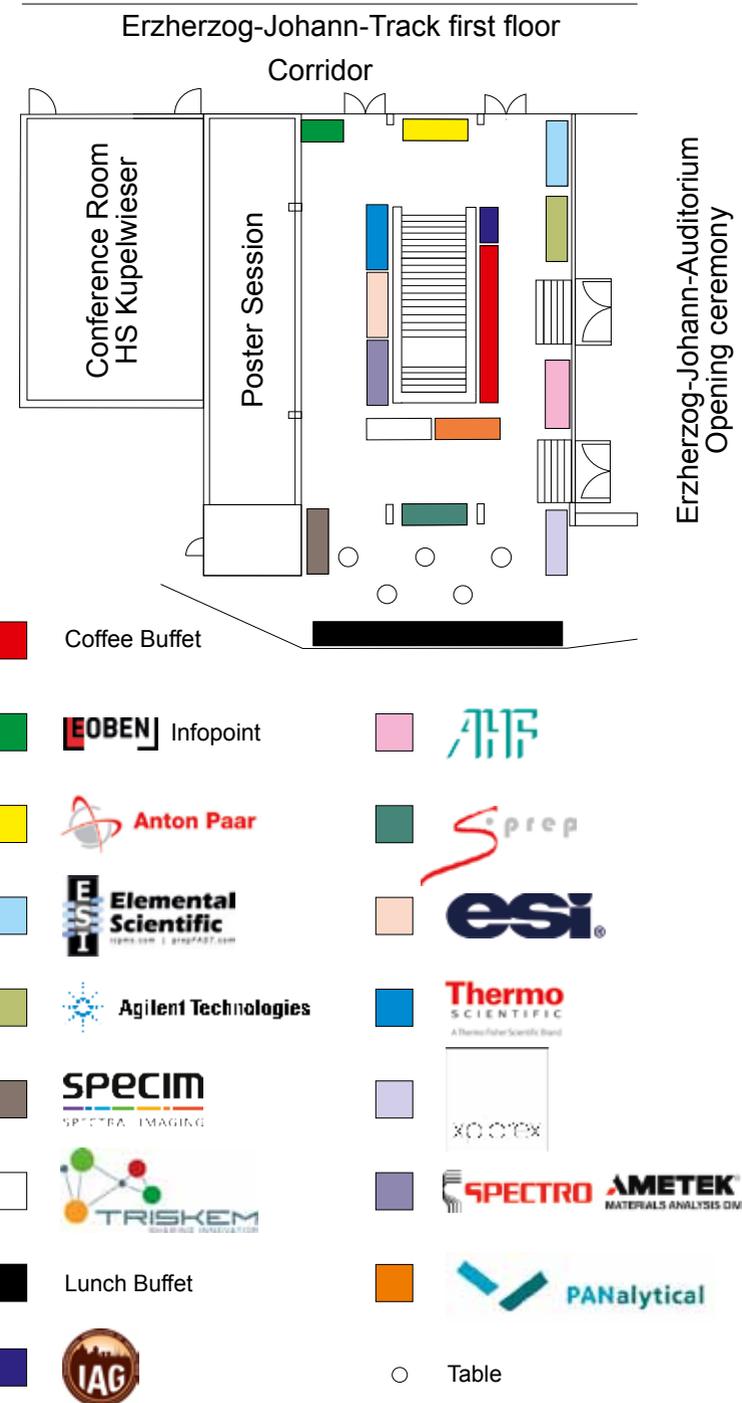
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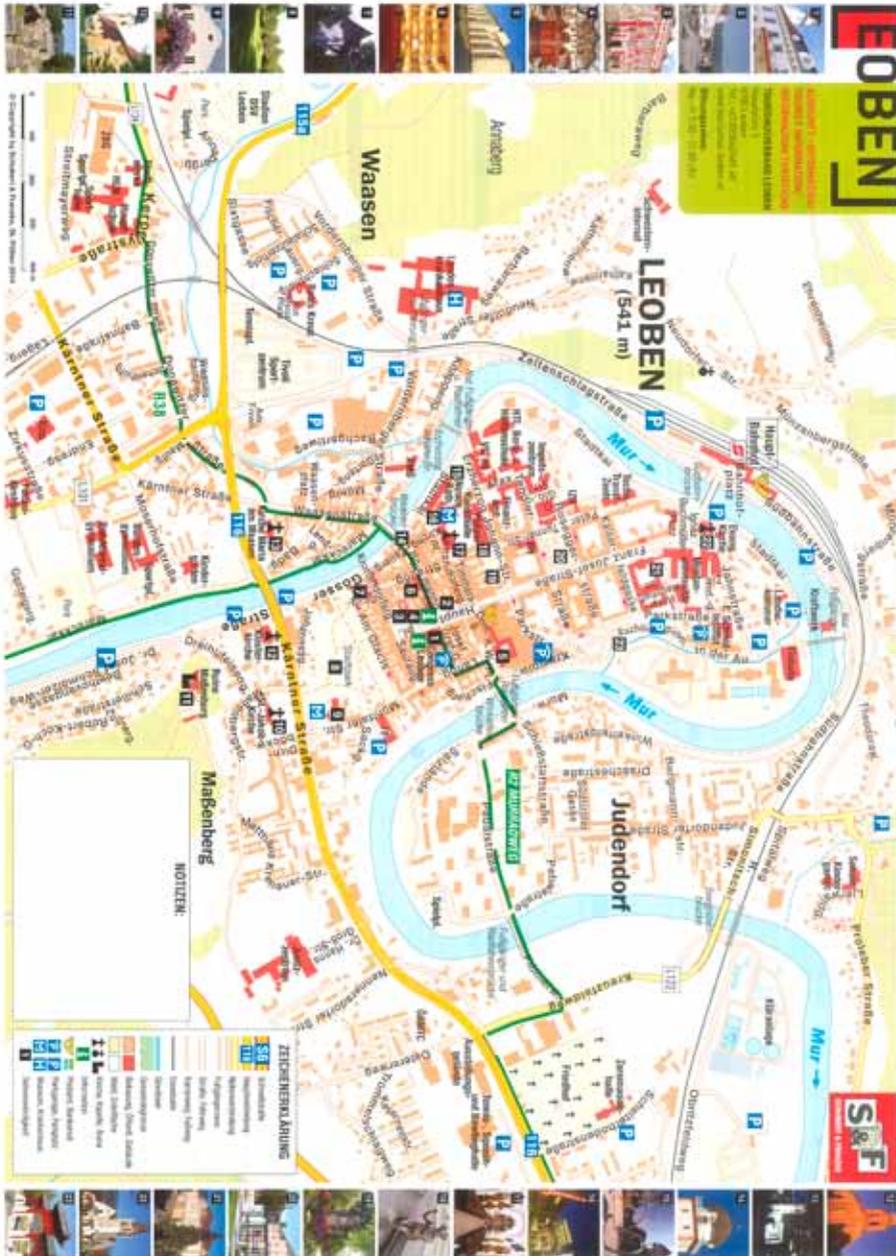


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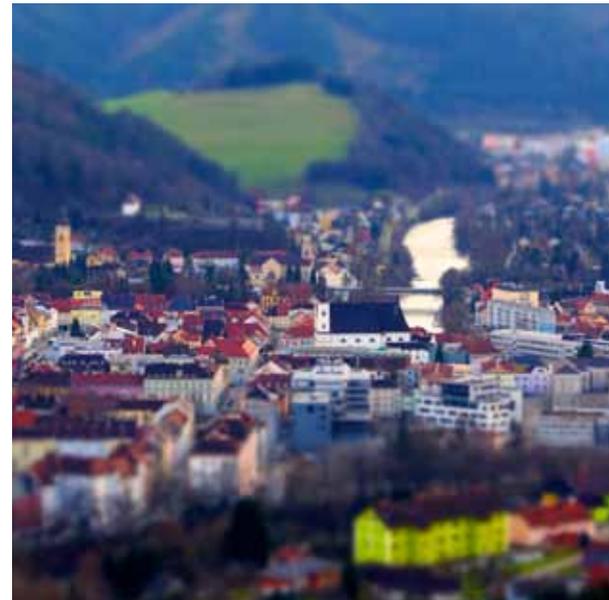
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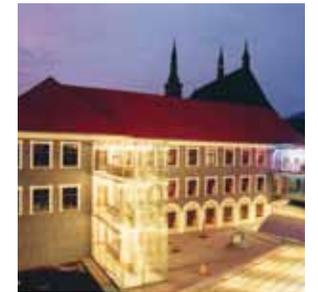
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PROGRAMME

Overview

	Sunday – 09/08	Monday – 10/08	Tuesday – 11/08	Wednesday – 12/08	Thursday – 13/08	Friday – 14/09
08:15						
08:30	Registration for Short Courses	Opening Ceremony	Announcements	Announcements		
08:40		Thomas Prohaska	Wolfgang Müller	Frank Melcher	Henry Longenrich	
09:00	Short Courses	Wilson Webb	Brand Ingham	Malitch Cupper	Garbe-Schönberg	
09:30	Refreshments	Begzsuren	Rachetti	Dias	Onuk	
10:10		Refreshments	Refreshments	Refreshments	Refreshments	
10:30		Gabler	Wünscher	Güllong	Belousov	
10:50		Kirkwood	Bokhari	Wiedenbeck	Macholdt	
11:00	Short Courses	Malitch	Zack	Renno		
11:20		Lunch Break - included	Lunch Break - included	Lunch Break - included	Lunch Break - not included	
12:00	Lunch Break - included for SC participants					
12:20		Wälle	Company Presentations			
12:40		Walkner				
13:00		Everett				
13:20	Short Courses	Havelcová				
13:40		Glass				
14:00	Refreshments	Petrakova	Posters and Exhibition			
14:20		Refreshments				
14:40	Short Courses	Moher				
15:00						
15:20						
15:40						
16:00						
16:20						
16:40						
17:00	Registration		IAAG General Meeting	Conference City Tour, Buschenschank		
17:20						
18:00		Gösser Brewery Tour, Göss				
19:00						
20:00	Welcome Reception		Classical Concert, Aula University			
21:00						
22:00						
23:00						

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Overview posters

Poster	Last Name	First Name	Title
P01	Almogren	Saad	Integration of Electrical Resistivity Tomography and GPR for Sinkholes Detection in Al-Rufa'a Area,
P02	Begzsuren	Davaasuren	Neutron activation analysis of urban soils from Mongolia
P03	Hamida	Diab	The reconstruction of paleo-environment Albo-Aptian sediments of the massive El Hmaima North Tébéssa
P04	Ismail	Esam	Impact of Heavy Metals Pollution on Continental Water Resources: a Case Study in El-Minia Province, north Upper Egypt
P05	Kepa	Luiza	Elemental analysis in archaeometric study of pottery of Yaz II culture from northern part of Serakhs oasis, south of Turkmenistan
P06	Pessoa	Jairo	Characteristics of marine Co-rich ferromanganese crusts of the South Atlantic through the distribution of the rare earth elements
P07	Rejas	Marta	Characterization of volcanic ashes from ~4200 BP Cerro Blanco eruption-Central Andes using LA-HR-ICP-MS and EPMA
P08	Suoranta	Terhi	Cloud point extraction for the determination of platinum group elements in moss samples by ICP-MS
P09	Navarro	Margareth	LA-SF-ICP-MS U-Pb zircon dating at University of Campinas, Brazil
P10	Nogueira	Leonardo	Carbon and oxygen isotopic geochemistry of paleoproterozoic carbonates from Fecho do Funil Formation – Iron quadrangle - Brazil
P11	Pribil	Michael	High precision in-situ Pb isotope analyses by LA-MC-ICP-MS using a USGS synthetic basalt glass (BPbISO-1) spiked with NIST SRM 981
P12	Santos	Anderson	Martin Vaz Island Ar-Ar dating, South Atlantic, Brazil
P13	Bank	Tracy	Detection of metals and rare earth elements in deep eutectic solvents and ionic liquids using ICP-MS
P14	Dressler	Sandra	Mineralogical and chemical analysis of secondary raw materials - challenges and pitfalls
P15	Hutchinson	Rob	SelfSeal sample chamber: automation for industrial bulk analysis
P16	Kiseleva	Daria	Raman investigation of human dental hard tissues affected with dental diseases of different etiology
P17	Stoll	Brigitte	Advantages and disadvantages of femtosecond 200 nm laser ablation- ICP-mass spectrometry for trace element analysis
P18	Rejas	Marta	Using portable X-Ray fluorescence to identify the K-Pg boundary in terrestrial records
P19	Durisova	Jana	Laser ablation ICP-MS study of trace elements from different deposit/mineralization types of molybdenite
P20	Elhabab	Adel	Geochemical and mineralogical characters of the coastal plain sediments of the Arabian Gulf, Kuwait
P21	Rahfeld	Anne	Geochemical and mineralogical analysis of Kupferschiefer
P22	Strnad	Ladislav	In situ trace element analysis of gem opals from Dubnik (Slovakia): Comparison of LA-ICP-MS and ICP-MS data
P23	Cook	Jennifer	Reference materials and an international proficiency testing programme for microanalytical laboratories
P24	Hutchinson	Rob	SelfSeal sample chamber: automation for industrial bulk analysis
P25	Krause	Joachim	Challenges and solutions on the major and trace element analysis of Eu-dialyte group minerals with the electron microprobe
P26	Osbahr	Inga	A novel approach for efficient identification and accurate chemical characterisation of platinum-group minerals by combining Electron Probe Microanalysis and Mineral Liberation Analysis
P27	Shin	Hyung Seon	Determination of rare earth elements in geological samples with radio-frequency glow discharge mass spectrometer
P28	Aasuren	Ariunbat	Certified reference materials of lithium ore produced at Central Geological Laboratory of Mongolia
P29	Bokhari	S. N. Hussain	Determination of Ru in OKUM and BIR-1 with sintering-anion exchange
P30	Bokhari	S. N. Hussain	Determination of Ru, Pd, Rh and Au in MUH-1 reference material with sintering-Te-co-precipitation with ID-ICP-MS
P31	Geraldes	Mauro	U-Pb and Lu-Hf calibration of the new LA-ICP-MS Multilab at Rio de Janeiro State University
P32	Geraldes	Mauro	Pb isotopic measurements in NIST 610 by LA-ICP-MS (Neptune)
P33	R. da Silva	Marcela	Quantification of trace and rare earth elements in samples of banded iron formations of the Quadrilátero Ferrífero, Brazil, aiming the production of reference material
P34	Savard	Dany	Concentration of metals and semi-metals in black shales: A new sequential protocol
P35	Weis	Ulrike	10 years GeoReM database
P36	Huang	Yunjie	Novel dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry for the determination of trace noble metals in geological samples
P37	le Roux	Petrus	Evaluation of whole-rock nano-particle pressed powder tablets for lithium and boron isotope analysis
P38	Okina	Olga	Microelements' determination in rocks by ICP-MS: problems of routine analysis
P39	Savard	Dany	LA-ICP-MS analysis of massive sulfides: progress towards a new calibration material
P40	Tupaz	Carmela Alen	Comparison of microwave plasma atomic emission spectrometry (MP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) for the determination of scandium from Philippine laterite samples

Sunday 09/08

Time	Activity		
08:15	Registration for Short Courses participants		
08:30			
08:40			
09:00	Portable XRF Instruments and Analysis Short Course	Fundamentals and Applications of LA-ICP-MS	
09:30			
09:50			
10:10			
10:30	Refreshments		
10:50			
11:00	Portable XRF Instruments and Analysis Short Course	Fundamentals and Applications of LA-ICP-MS	
11:20			
11:40			
12:00			
12:20	Lunch Break		
12:40			
13:00	Portable XRF Instruments and Analysis Short Course	Fundamentals and Applications of LA-ICP-MS	The GeoPT Proficiency Testing Programme
13:20			
13:40			
14:00			
14:20	Refreshments		
14:40			
15:00	Portable XRF Instruments and Analysis Short Course	Fundamentals and Applications of LA-ICP-MS	The GeoPT Proficiency Testing Programme
15:20			
15:40			
16:00			
16:20	Registration		
16:40			
17:00	Welcome Reception		
18:00			
19:00			
20:00			
21:00			

Registration Geoanalysis 2015

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Monday 10/08

Time	Activity	
8:15	Opening Ceremony	
8:40	Thomas Prohaska	Isotopes as Tracers in Archaeological Sciences
9:30	Wilson	BPbISO-1G, a synthetic geologic glass designed to facilitate lead isotopic analysis in geologic materials
9:50	Webb	Systematic bias in the reporting of XRF results for trace elements at concentrations approaching the detection limit — evidence from the GeoPT proficiency testing programme
10:10	Begzsuren	Testing schemes organized at Central Geological Laboratory of Mongolia
10:30	Refreshments	
11:00	Gäbler	Analytical fingerprint of wolframite: Chemical analysis, data variability, statistics
11:20	Kirkwood	Stream sediment geochemistry as a tool for enhancing geological understanding: An overview of new data from south west England
11:40	Malitch	Radiogenic and stable isotope study of the Vologochan and Mikchangda ore-bearing intrusions of the Noril'sk Province: Implications for exploration
12:00	Lunch Break	
13:20	Wälle	Analysing fluid inclusions by laser ablation sector field ICP-MS – advantages of higher sensitivity
13:40	Walkner	Trace element quantification in crude oils using ICP-QQQ-MS
14:00	Everett	Influences on the distribution of hydrothermally enriched commodity elements in stream sediments of south west England, investigated using new geochemical baseline survey data
14:20	Havelcová	Geochemistry of anomalous uranium enrichment in fossil resin
14:40	Glass	Sampling of moisture content in particulate materials
15:00	Petrakova	Determination of organic-mineral composition of bazhenov formation rocks (West Siberia, Russia) by combination analytical technique
15:20	Refreshments	
16:00	Moher	Application of ASTER data in the genesis and Genetic relationship of Barite and Iron Ores in El- Bahariya Oasis Western Desert Egypt

Tuesday 11/08

Time	Activity	
8:30	Announcements	
8:40	Wolfgang Müller	Time-resolved isotopic and elemental analysis of teeth (LA-(MC) ICPMS, SIMS) in archaeometry/forensics – examples related to the Iceman and medieval Ag-mining
9:30	Brand	Performance comparison of portable XRF instruments: A mineral exploration industry perspective
9:50	Ingham	Calibration strategies for geo-environmental XRF analysis
10:10	Rachetti	Problems with elements not included in the software of handheld XRF analysers
10:30	Refreshments	
11:00	Wünscher	Analysis of rare earth elements in soils and sediments
11:20	Bokhari	Removal of Interferences on platinum in Platinum Group Elements (PGE) reference materials (RM)
11:40	Zack	Principles of LA-QQQ-ICP-MS and opportunities in Earth Sciences
12:00	Lunch Break	
13:20	Company Presentations	
14:20	Posters and Exhibition	
16:40	IAG General Meeting	

Wednesday 12/08

Time	Activity	
8:30	Announcements	
8:40	Frank Melcher	Fingerprinting of conflict minerals: the coltan case
9:30	Malitch	Radiogenic and stable isotope study of the Vologochan and Mikchangda ore-bearing intrusions of the Noril'sk Province: Implications for exploration
9:50	Copper	Application of luminescence dating and lead isotope analysis to authenticate and provenance a bronze artefact from northern Australia
10:10	Dias	Absolute calibration for the EMPA-FT
10:30	Refreshments	
11:00	Guillong	Careful validation of U-Th zircon dating by LA-ICP-MS
11:20	Wiedenbeck	Performance Capabilities of the Cameca 1280-HR SIMS Instrument
11:40	Renno	What role can and should play ion beam analytical methods in the context of geometallurgy?

Thursday 13/08

Time	Activity	
8:40	Announcements	
9:00	Henry Longerich	Inductively coupled plasma mass spectrometry: A personal odyssey; trials, tribulations, problems, and successes
10:10	Garbe-Schönberg	Particle size matters: A new strategy for manufacturing microanalytical reference standards from nano-particulate powder pellets
10:30	Onuk	Development of the matrix-matched sphalerite (ZnS) standards MUL-ZnS-1 and MUL-ZnS-2 for in-situ analysis of trace elements by laser ablation inductively coupled plasma-mass spectroscopy (LA-ICP-MS)
10:50	Refreshments	
11:20	Belousov	Comparison of ablation of different sulphides as a function of the type of nano-second pulse width laser ablation system
11:40	Macholdt	The search for suitable reference materials for microanalytical analyses of Mn rich samples
12:00	Lunch Break	
14:00	Ramsey	Characterizing isotopic homogeneity of candidate reference materials at the picogram sampling scale
14:20	Enzweiler	Revisiting the chromium reference value in BRP-1 (Basalt Ribeirão Preto)
14:40	Wilson	BPbISO-1G, a synthetic geologic glass designed to facilitate lead isotopic analysis in geologic materials
15:00	Bank	Optimization of rare earth analyses in geologic material using universal cell technology and ICP-MS
15:20	Jochum	Reference values following ISO guidelines for 20 most frequently requested rock reference materials
15:40	Closing Ceremony	

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Isotopes as Tracers in Archaeological Sciences

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*currently research scientist at the Helmholtz Center Geesthacht, Germany

²Natural History Museum Vienna, Department of Anthropology, Vienna, Austria

Archaeometry relates to the question: *What happened in the past and can we trace it?* Analytical techniques have been developed and applied to investigate materials in a historic context, including e.g. dating methods, conservation science, the investigation of archaeological artifacts or skeletal remain in biological anthropology or archaeozoology.

In this context, isotope ratio analysis has gained significant importance since isotopic systems are known to preserve a variety of information: Besides dating, isotopes are used to shed light on past environmental conditions, living conditions of animals and humans, migration and movements or to proof authenticity or origin of skeletal remains or archaeological artifacts. Light stable isotopes are mainly used as environmental parameters or give information about biological systems (e.g. the nutritional status of a human). Recently, also new 'non-traditional' isotopic systems (e.g. Li, B, Si, S, Mg, Ca, Sb) have gained importance to reveal information about the environmental past (temperature, humidity, pH of aquatic systems, volcanic activities, weathering – just to name a few). Sr and Pb stand out in archaeological science as indicators of authenticity and origin. Pb isotopes are of particular interest in order to trace goods (glass, ceramics or metals) whereas Sr is a renowned indicator for calcified biogenic matter (human and animal skeletal remains but also corals, fish hard parts, shells). Novel isotopic systems used for origin and authenticity studies are Cu, Zn, Sn, Nd and Sb.

Sr isotopes are of particular significance in mobility and migration studies of humans and animals due to their outstanding properties (e.g. significant

geogenic variation of the radiogenic ⁸⁷Sr of different Sr sources and resulting regional differences), the ubiquity of Sr in nature and the chemical similarity of Sr to Ca. Above all, many calcified biological matrices (e.g. teeth, corals, mussel shells) show a clear time-resolved growth. In case of humans, tooth enamel and dentine incorporate the Sr fingerprint via the ingestion of food at different stages during the life and thus can be used to investigate autochthony and allochthony. Laser ablation coupled to elemental and isotopic mass spectrometers has become an important method in these studies.

One major challenge in mobility and migration studies of humans and animals is the identification of an autochthonous Sr isotopic range (i.e. the Sr, that is taken up by the autochthonous individual via their nutrition), to which the Sr isotopic composition of bones and teeth are compared to in order to judge provenance. In a new approach, the autochthonous signal is calculated by estimating nutritional sources via isoscapes from possible regions of provenance of singular food commodities by using ArcGIS.

Selected examples on different Austrian excavation sites, which were investigated in collaboration with the Natural History Museum Vienna, will illustrate the potential of isotope ratio research.

Time-resolved isotopic and elemental analysis of teeth (LA-(MC) ICPMS, SIMS) in archaeometry/forensics – examples related to the Iceman and medieval Ag-mining

WOLFGANG MÜLLER¹, KURT ALT², ROBERT ANCKIEWICZ³, SAMUEL BARRETT¹, LUCA BONDIOLI⁴, KLAUS OEGGL⁵, VIOLA WARTER¹, IAN WILLIAMS⁶

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³Institute of Geological Sciences, Polish Academy of Sciences, Krakow, Poland

⁴Sezione di Bioarcheologia, Museo Nazionale Preistorico Etnografico 'L. Pigorini', Rome, Italy

⁵Institute of Botany, University of Innsbruck, Austria

⁶Research School of Earth Sciences, The Australian National University, Canberra, Australia

Mammalian teeth mineralize over several years (e.g. ~15 years in humans) and record the ambient environment via the ingested nutrition. Teeth are an extraordinary archive for the reconstruction of various ecological parameters, including mobility, exposure to toxic metals or dietary shifts. Sub-annual time-resolution can easily be achieved if the information in sequentially forming teeth is extracted at sufficient resolution. Spatially-resolved isotope ratio and elemental microanalysis by laser-ablation or secondary-ion mass spectrometry (LA-(MC) ICPMS, SIMS) are suitable techniques for Sr and O-isotope and trace element analysis at the μm (sub-mm) scale, respectively. Natural Sr-isotopic variation occurs due to changing rock types (soil) (e.g. [1]), whereas the O-isotopic composition of precipitation varies systematically between the seasons. These input signals get incorporated into enamel bioapatite, where compositional (isotopic/elemental) signals may however get attenuated by the complex two-stage enamel mineralization process, whose effect can be

minimized by the specific sampling strategies applied - showcased here via two different examples.

Firstly, the surprising discovery in 1991 of an exceedingly well-preserved human mummy in the Alps, the Neolithic Alpine Iceman, enabled unprecedented insights into past living conditions, derived from both his equipment and the mummy itself (e.g. [1]). However, the social role of the Iceman has remained uncertain, even though his involvement in some form of early transhumance has become one favoured hypothesis [2, 3]. However, this has been questioned recently on the basis of pollen in animal dung found at the Iceman's discovery site [4] and regional pollen profiles [5]. Vertical transhumance is a subsistence strategy typical of many mountain ranges including the European Alps, but it remains unclear when this form of landscape use started to be practised in the Alps [6]. We use animal teeth (mostly cattle, few sheep/goat) from several sites close to the Iceman's discovery site in N Italy (South

Tyrol/Alto Adige), spanning the Late Neolithic to the Late Bronze Age, to directly evaluate intra- and intertooth variability of their enamel Sr and O isotopic compositions. In some cases, pairs or triplets of sequentially forming molars of one individual allow a continuous assessment of 2-3 years of that animal's life. We find that many teeth show remarkable intra-tooth Sr isotopic variability resembling cyclic variations which imply regular changes in grazing location. Crucially, SIMS (SHRIMP) in-situ $\delta^{18}\text{O}$ profiles help identify summer/winter growth domains and the degree of seasonality. The variable local geology is assessed via the bioavailable Sr-isotopic composition of non-anthropogenically influenced grass samples in order to evaluate whether local only or more regional (transhumance) mobility is recorded.

Secondly, in-vivo Pb-exposure and (im)migration into a medieval Pb-Ag mining community from SW Germany (Black Forest) [7, 8] can be quantified via compositional and Sr-O isotope profiles of tooth enamel, facilitated by its resistance to post-mortem diagenetic alteration despite widespread Pb contamination of local soils. In-vivo inter-tooth and particularly peak-like intra-tooth Pb concentration variations exceed three orders of magnitude even for the same individual, which in some cases correlate with equally contrasting Sr-isotope profiles, confirming immigration from non-polluted areas. Detailed timing is available from enamel histological analysis and taken together such investigations get closer to 'writing biograph(ies) at the edge of history' [9]. Corresponding results will be presented.

[1] Müller, W., *et al.*, Origin and Migration of the Alpine Iceman. *Science*, 2003. 302: p. 862-866.

[2] Spindler, K., *Der Mann im Eis. erweiterte Taschenbuchausgabe* ed2000, München: Goldmann Verlag. 416.

[3] Bortenschlager, S., *The Iceman's environment*, in *The Iceman and his natural environment* 2000, Springer. p. 11-24.

[4] Oeggl, K., A. Schmidl, and W. Kofler, Origin and seasonality of subfossil caprine dung from the discovery site of the Iceman (Eastern Alps). *Vegetation History and Archaeobotany*, 2009. 18(1): p. 37-46.

[5] Festi, D., A. Putzer, and K. Oeggl, Mid and late Holocene land-use changes in the Otztal Alps, territory of the Neolithic Iceman "Otzi". *Quaternary International*, 2014. 353: p. 17-33.

[6] Gleirscher, P., *Almwirtschaft in der Urgeschichte. Der Schlern*, 1985. 59: p. 116-124.

[7] Alt, K.W., *et al.*, Infant osteosarcoma. *International Journal of Osteoarchaeology*, 2002. 12(6): p. 442-448.

[8] Alt, K.W., *et al.*, Die mittelalterliche Bergbaubevölkerung des 12. Jahrhunderts von Sulzburg, Kr. Breisgau-Hochschwarzwald. *Anthropologische und archäometrische Studien. Freiburger Beiträge zur Archäologie und Geschichte des Ersten Jahrtausends* 2008: VML Verlag Leidorf. 156.

[9] Fleming, R., *Writing Biography at the Edge of History. American Historical Review*, 2009. 114(3): p. 606-614.

Fingerprinting of conflict minerals: the coltan case

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Since about the year 2000, the African continent has developed into a major exporter of coltan from rare-element pegmatites and their eluvial and alluvial weathering products. Coltan – an important tantalum source - is a central African trade name of mineral concentrates chiefly composed of members of the columbite-tantalite group [(Fe,Mn) (Nb,Ta)₂O₆], with additional tapiolite, wodginite, ixiolite, microlite, cassiterite, rutile and other heavy mineral phases. Tantalum is a rare metal whose strength, chemistry and electronic properties make it valuable in many high technology and medical applications. The use of tantalum has, for instance, been instrumental in reducing the size of mobile phones.

Although the major resources of tantalum are located in Australia, Brazil and Canada, African countries account for more than 75 percent of the current world production (2013: 1,230 metric tons Ta₂O₅), and artisanal and small-scale mining of coltan is essential to many local economies. Probable links between raw material exports and continuing violent conflicts, especially in the Democratic Republic of the Congo (DRC), are widely discussed. On behalf of the German Federal Ministry for Economic Cooperation and Development (BMZ), the Federal Institute for Geosciences and Natural Resources (BGR) commenced a pilot project to test the general viability of a traceability system that would proof the origin of coltan. Such a system would allow ore produced within

regions affected by civil war to be distinguished from other sources.

Combined mineralogical, geochemical and geochronological signatures of columbite-tantalite ores are used to trace the origin of ore concentrates. The chemical composition of Nb-Ta oxides in pegmatites and rare-element granites is characterised by a strong variability. However, major as well as trace elements show regional characteristics that, in many cases, allow for the distinction of ore provinces based on the composition of a representative number of grains. The major element variations in columbite-tantalite, tapiolite, wodginite and ixiolite reflect differentiation of, and fractional crystallization from melts. The degree and type of the variation of trace element concentration in Nb-Ta oxides is complex and depends on multiple factors, including crystal-chemical parameters (e.g., ion radius, charge), melt chemistry (e.g., presence of fluxing elements), internal differentiation of the melt, reaction with host rocks, and melt source characteristics. All these factors are superimposed on each other and result in characteristic trace element signatures for Nb-Ta oxides from different ore provinces.

About 15,000 electron microprobe and ca. 10,000 LA-ICP-MS datasets from rare element pegmatite and rare metal granite deposits ranging in age from the Archean to the Mesozoic and covering all continents

except Antarctica were evaluated and demonstrate variations over two to four orders of magnitude for most trace elements. The most important minor elements in columbite-tantalite are Ti, W, Zr and, Sn (median for the dataset is > 1000 ppm), followed by U, Hf (100-500 ppm), Al, Mg, Pb (10-100 ppm), Sc, Li, Mo, Y, Th and, Tl (1-10 ppm). The median concentrations of the REE, As, Sb, Bi, and Sr are below 2 ppm, and concentrations of Be, Rb and Ba in CGM are usually below the detection limit of the LA-ICP-MS method.

Considering the coltan “fingerprint” for ore concentrates originating from the African continent, the determination of mineral formation ages using the U-Pb isotope system traces the origin of a concentrate to one out of five “age provinces” known from African tantalum-bearing pegmatites, i.e. >2.5 Ga, 2.0 Ga, 0.9-1.0 Ga, 0.5 Ga and <0.3 Ga. Mineralogical and geochemical attributes of coltan concentrates and columbite-tantalite group minerals further allow distinction of single deposits within a given province. Using appropriate statistical tests, similarities and dissimilarities between coltan concentrates are calculated. The coltan fingerprinting method has become an integral part of a mineral certification scheme that is currently being installed in the Great Lakes Region of Central Africa.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: A PERSONAL ODYSSEY; TRIALS, TRIBULATIONS, PROBLEMS, AND SUCCESSES.

HENRY P. LONGERICH

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I have published several reminiscences (Longerich, 1995, 2001, 2004, 2012) of my scientific life following my personal "discovery" of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in 1983 at the American Society of Mass Spectrometry convention in Boston where I met Alan Gray, Alan Date, and Don Douglas, leaders in the development of ICP-MS. Alan Date of the British Geological Survey was had a significant effect on the early bringing of ICP-MS to the attention of the geoanalytical community. These personal stories were all named "Odysseys" after Homer's classic story of Odysseus "ten years of wandering in the wilderness" as wandering seemed to describe the first years of ICP-MS, and later years after we interfaced Laser Ablation sampling to the ICP-MS. This lecture will review this history, noting the tremendous effect that ICP-MS has had on geoanalytical elemental analysis as ICP-MS nearly doubled the number of elemental analytes routinely available to geologists.

From the first days of ICP-MS it was noted that isotopic analysis was possible with ICP-MS which was first reported by Alan Date and in our first ICP-MS publication (Strong and Longerich, 1985) we reported some Pb isotopic results. Later when multi-collector instruments became available the

number of isotopic systems available to the geological community approximately doubled. This is due to the ability of the ICP to ionise elements which have high ionisation potentials which can not be determined using Thermal Ionisation-Mass Spectrometry (TI-MS), and the availability of external calibration paradigms in ICP-MS which are very difficult to implement in TI-MS. The ease of measuring important between element isotope ratios is also an additional powerful capability of ICP-MS.

In 1988, we decided to investigate Laser Ablation (LA) sample introduction. Alan Grey (1985) first reported LA-ICP-MS measurements. We configured a system from components since at that time there were no commercially available LA systems. Especially important was the incorporation of petrographic quality microscope optics, an essential capability not appreciated by the instrument companies at that time. Our land mark paper (Jackson, *et al.*, 1992) demonstrated the tremendous power of the technique for geological micro analysis, along with several weaknesses which we later minimised.

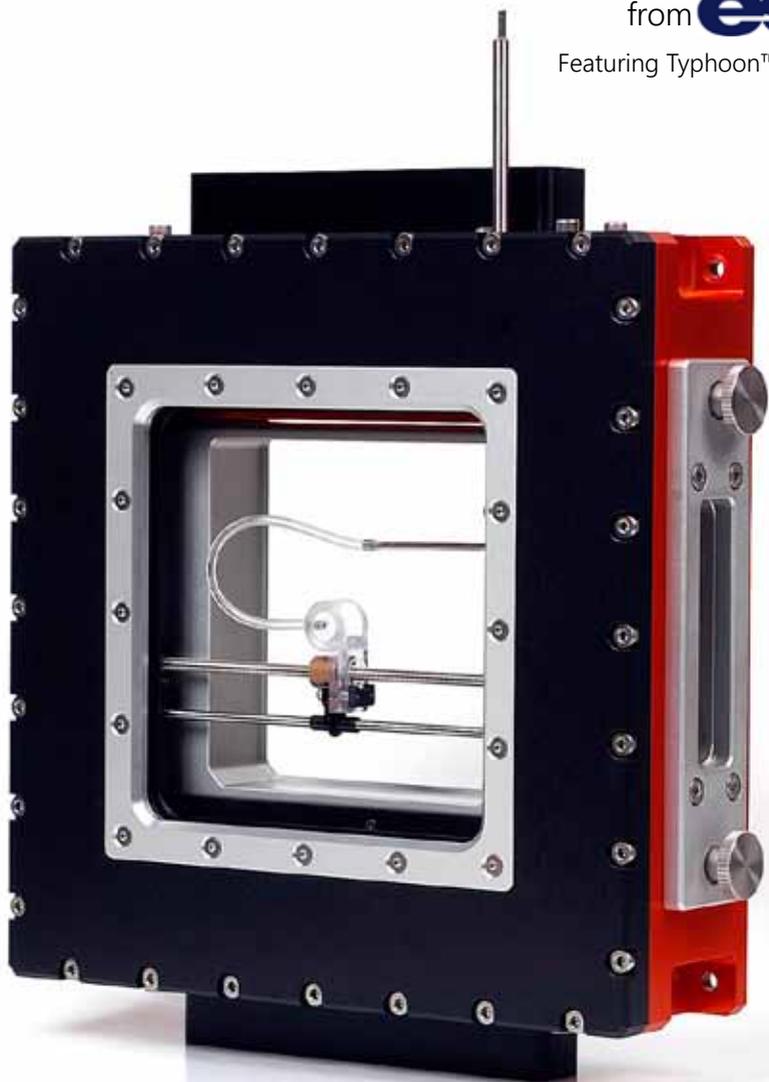
This talk will emphasise the fun and satisfaction of these early days of research and development of ICP-MS. And finally will end with some words to live by.

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ORAL PRESENTATIONS

OP-01**Development of quality control materials from natural geologic starting materials****STEPHEN WILSON¹, PETER WEBB, PHIL POTTS**¹United States Geological Survey, Denver (USA)

Geologic laboratories involved in mineral exploration and environmental monitoring are constantly faced with the need for reliable quality control materials (QCMs) covering a wide range of elements at diverse concentration ranges. To mitigate the need for quality control programmes using dozens of established reference materials the USGS and IAG collaborated in the development of specialized QCMs covering the majority of the periodic table at concentrations levels 2-100 times common laboratory determination limits. Soil and sediment materials were collected from seven current or historic mining sites in the western United States known to contain elevated concentrations

of trace elements. Materials from these sites were combined to produce QCMs at three concentration levels which were designated SdAR-L2 (Low), SdAR-M2 (Medium) and SdAR-H1 (High). Chemical analysis of the starting materials combined with a USGS blending programme allowed the customization of the final blend which minimized the number of elements below detection limits. Discussions will focus on sample site selection, the preparation strategy and the use of the GEOPT proficiency testing programme to develop certificate values. Examples of some key elements are presented in table 1.

Table 1. Selected element concentration (mg/kg) in SdAR materials

Element	SdAR-L2	SdAR-M2	SdAR-H1
Ag	2.4	15	76
As	15	76	396
Cu	48	236	1159
Hg	0.3	1.44	7.3
Pb	180	808	3893
Sb	18	107	505
Tl	0.98	2.8	11.1
Zn	210	760	3684

OP-02**Systematic bias in the reporting of XRF results for trace elements at concentrations approaching the detection limit — evidence from the GeoPT proficiency testing programme****PETER WEBB¹, PHILIP J. POTTS¹, MICHAEL THOMPSON**¹Walton Hall, Milton Keynes (UK)

The GeoPT proficiency testing programme provides a large body of data for geological materials derived from a variety of analytical techniques. Examination of elemental concentration distributions shows that XRF results for many trace elements (for example As, Bi, Cd, Mo, Sn, Ta and W) are frequently highly variable at concentrations approaching detection limits and often demonstrate significant positive

bias. Some of the factors thought to contribute to these observations will be reviewed. We advise XRF analysts to be cautious when reporting values close to detection limits: they should give careful consideration to the extent of uncertainties, the potential for bias and whether the results satisfy their fitness for purpose criteria.

OP-03**Proficiency testing schemes organized at Central Geological Laboratory of Mongolia**

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Central Geological Laboratory (CGL) of Mongolia, besides analytical work on geological, mining and environmental samples for its around 60 years history, has been working on production of certified reference materials/reference materials (CRM/RM) from many kinds of mineral resources since 1970s.

During this period the CGL has produced more than 60 CRM for geological materials that are certified as international and national, as well as institutional RM in accordance with relevant standards. Also the CGL has been intensively developing international cooperation in this field. For instance, it has produced 5 CRM together with IAG and one with BGR, Germany.

Since 2012, the CGL has been accredited as a Reference material producer against ISO Guide 34 by the ACLASS ANSI-ASQ National Accreditation Body (ANAB, the new home of ACLASS and FQS since 2015).

Based on experiences, skills, techniques and technologies of production of CRM/RM, the CGL has set a goal to become a Proficiency testing provider since 2013, and has updated its quality management system in accordance with ISO/IEC 17043. It is planning to organize proficiency testing schemes twice per year.

In 2014, the CGL successfully organized the first proficiency testing scheme CGL PT01-Coal within laboratories operating in Mongolia. Copper ore was chosen as a proficiency testing sample for the next scheme based on feedbacks from participants and other laboratories operating in Mongolia.

The CGL is working to improve its proficiency testing programme by learning from other proficiency testing providers.

OP-04**Analytical fingerprint of wolframite: Chemical analysis, data variability, statistics**

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The analytical fingerprint method (AFP) is a scientific tool to verify the documented origin of cassiterite, coltan, and wolframite ((Fe,Mn)WO₄) ore concentrates. Cassiterite, coltan, and wolframite plus gold are termed 'conflict minerals' as trading and illegal taxation are used to fund armed conflicts (e.g., in the eastern Provinces of the Democratic Republic of the Congo).

AFP of wolframite shall be applied as an optional tool within the framework of mineral certification. Mineral certification is a document-based mechanism which goes beyond the documentation of origin and includes other issues like social standards as well as occupational safety and health. The application case for the AFP of wolframite is given if the documented origin of a wolframite shipment is questioned and additional document-independent information is needed. The task of AFP is to provide evidence whether the questioned shipment originates from the documented origin or not. This can be done by comparing the analytical data of the shipment in question with data from samples of known origin stored in a reference database. The critical parameter for the AFP of wolframite is the distribution of major and trace element concentrations obtained from about 50 wolframite grains per ore concentrate. The chemical composition of single grains is analysed by LA-ICP-MS. Scanning electron microscopy with automated mineralogy (SEM-MLA) is used to define target grains for laser ablation. The wolframite database available at BGR is continuously extended and comprises more than 92 ore concentrates from 49 mine sites which sum up to more than 4580 analyzed wolframite grains.

The challenge to meet is how to define the 'similarity' of two samples (the sample in question and the reference sample(s) from the database) keeping in mind the natural variability of single ore bodies and the fact that the obtained wolframite concentrate samples are not taken representatively from the ore body. Wolframite grains from a single mine site exhibit chemical compositions which are highly variable and show nonparametric statistical distributions. But the range of this variability seems to be characteristic for a particular ore body. So, the distributions of major and trace element concentrations in different wolframite concentrates from one mine site should be similar to each other.

For each element the Kolmogorov-Smirnov statistic (KS-d) is chosen for the pairwise comparison of empirical distribution functions. Per definition the KS-d varies between 0 and 1; small KS-d indicates high similarity of investigated distributions and vice versa. For each pairwise comparison one KS-d value is calculated per element. As a measure of similarity of two wolframite concentrates a naïve approach is used by just summing up the KS-d values for all elements. A sample in question is compared to all samples of the database and the samples of the database are ranked according to their KS-d sum. Samples from the database with small KS-d sums are supposed to be more similar to the sample in question than samples with higher KS-d sums. This approach was applied for mine sites in Rwanda and empirical threshold values for the assessment of similarity have been deduced and tested.

OP-05**Stream sediment geochemistry as a tool for enhancing geological understanding: An overview of new data from south west England****CHARLIE KIRKWOOD¹, PAUL EVERETT, BOB LISTER**¹ British Geological Survey, Environmental Science Centre, Keyworth, Nottingham (UK)

Since 1967 the British Geological Survey has been collecting and analysing stream sediment samples from across Great Britain as part of the Geochemical Baseline Survey of the Environment (G-BASE) project. G-BASE data for south west England has become available following the completion of fieldwork in the area in 2012. With 52 elements analysed by laboratory XRF, at an average sampling density of one sample per 2.5km², this dataset allows the distribution of elements in the surface environment of south west England to be observed in great detail.

The geology of south west England is diverse: The present day bedrock consists of a spectrum of lithostratigraphic formations which preserve various stages of the region's Paleozoic tectonic cycle from passive margin to collisional orogenesis and subsequent erosion. This great geological diversity, the result of a broad range of sedimentary, metamorphic and magmatic processes, makes south west England an ideal study area for the investigation of relationships between all aspects of geology and surface geochemistry. This study focusses exclusively on the behaviour of elements whose distributions in stream sediments in south west England can be observed to be primarily lithostratigraphically constrained.

In this study we use a quantitative approach to identify the most notable geochemical characteristics of sediment samples overlying each of the sixteen lithostratigraphically unique spatial domains into which we classify the region. The most notable geochemical characteristics are explained in relation to the geological setting and key aspects of the composition of each domain. In cases where the documented geological properties of a domain are insufficient to account for the geochemical characteristics of the stream sediment samples overlying each domain, the geochemical data is offered as new evidence from which explanatory geological interpretations can be made.

The use of the stream sediment geochemical data for making geological interpretations in this way is supported by the innate strength of the relationships between stream sediment geochemistry and bedrock geology in the region, which we demonstrate visually with the aid of principal component analysis. Appreciation of the strength of these stream sediment geochemistry-bedrock geology relationships advocates G-BASE stream sediment data as a highly sensitive tool to aid quantitative mapping techniques and to improve geological interpretations.

OP-06**Compositional and isotope study of Ru-Os-Ir-Pt alloys and Ru-Os sulfides from the Witwatersrand Basin (South Africa): New data****KRESHIMIR MALITCH¹, INNA BADANINA¹, ROLAND MERKLE²**¹ Institute of Geology and Geochemistry, Ural Branch RAS, Ekaterinburg (Russia)² University of Pretoria (South Africa)

The Late Archean paleoplacers of the Witwatersrand Basin (South Africa) are not only unparalleled in their gold-uranium deposits, but are also a leading source for osmium production as a by-product of gold mining from rocks underlying the Ventersdorp Supergroup, which is about 2.7 Ga old (Altermann and Lenhardt 2012). Although the exact ages of platinum-group minerals (PGMs) in the Witwatersrand basin are not well constrained (only samples from the Kimberly Reef have been investigated using modern techniques; Malitch and Merkle 2004; Dale *et al.* 2010), it stands to reason that PGMs older 2.7 Ga must have formed before the deposition of the sediments in which they occur today.

The compositionally diverse PGMs from the Evander Goldfield, situated in the eastern extremity of the Witwatersrand Basin, have been studied by a number of modern techniques including SEM, EPMA and LA-ICP-MS. The characteristic feature of PGMs from Evander is an extensive presence of Ru-rich alloys (i.e., (Ru,Os,Ir), (Ru,Os,Pt,Ir), (Ru,Ir,Pt), (Ru,Pt)), which prevail over iridium, rutheniridosmine, Ru-Os

sulfides, Pt-Fe, Pt-Ru-Fe and Pt-Ir-Os alloys and other PGMs. The diversity of unnamed polycrystalline alloys of the system Ru-Os-Ir-Pt(±Fe) is in basic accordance with the fractionation trend proposed by Feather (1976). Equilibrium phase-relationships of osmium and ruthenium alloys at Evander, based on the restricted solid solution in the binary systems Os-Ir, Os-Ru and Ir-Ru (Massalski 1993), and the presence of a ruthenium-enrichment trend in Os-Ru-Ir-Pt alloys, are indicative of high temperatures and pressures, which could only be reached under mantle conditions. The Os-isotope results identify a restricted range of ¹⁸⁷Os/¹⁸⁸Os values (0.10481–0.10485) for coexisting Os-rich alloy and erlichmanite pairs that form primary PGM assemblage. Unradiogenic ¹⁸⁷Os/¹⁸⁸Os values are clearly indicative of a subchondritic mantle source of the platinum-group elements (PGE). The compositional and isotope data imply that the source for the PGMs was the Archean mantle, slightly differentiated with respect to PGE.

The study was supported by Russian Fund for Basic Research (grant 15-05-08332).

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OP-07**Analysing fluid inclusions by laser ablation sector field ICP-MS – advantages of higher sensitivity****MARKUS WÄLLE¹, CHRISTOPH A. HEINRICH**¹Institute of Geochemistry and Petrology, Zürich (Switzerland)

Fluid inclusions are important tracers of ancient hydrothermal events like e.g. ore formation and their contents may shed light on the those processes. LA-ICP-MS has proven to be a useful tool to determine the major and trace elemental composition of fluid inclusions (Heinrich *et al.* 2003). However, the mass content of fluid inclusions is limited and smaller inclusions occur normally more often than bigger ones, requiring high sensitive instruments for detection of trace element concentrations like gold, where concentrations of interest often are in the low or even sub ppm-range. In addition, plasma based interferences are a severe issue for determining low concentration of some rock form elements like calcium and iron (e.g. a few µg/g or lower) by LA-ICP-MS in fluid inclusions.

Sector field (SF-) ICP-MS instruments provide a higher sensitivity than normal quadrupole (Q-) ICP-MS at the cost of a slower scanning speed when scanning over the entire elemental mass range, i.e. when changes of the magnet settings are involved. The performance of a SF-ICP-MS (Element XR) was investigated with a set of fluid inclusions in quartz with a salinity of 4wt% and a menu of 21 elements from ⁷Li to ²⁰⁸Pb.

The 20% longer scan time compared to a Q-ICP-MS (Elan 6100 DRC) led within error to the same concentrations by a ten time lower detection limit for high mass elements like gold.

The instrument types over different ways to get rid of plasma based interferences. The medium mass resolution on a SF-ICP-MS is sufficient to resolve ⁴⁰Ar¹⁶O+ on ⁵⁶Fe+. However, the mass resolution required to separate ⁴⁰Ca+ from ⁴⁰Ar+ is beyond the scope of those instruments. Unfortunately, a higher mass resolution results in reduced sensitivity and the switching time of one second between different resolutions is too long to change it during the measurement of an inclusion signal. Chemical resolution by a dynamic reaction cell (DRC) on a Q-ICP-MS is able to get rid of both interferences (Günther *et al.* 2001). However, an reduction in sensitivity or the introduction of additional interferences can occur while applying a DRC. In this study, we also investigate the benefit and drawbacks of chemical or higher mass resolution to measure concentrations of element which suffer from plasma interferences in fluid inclusions while keeping the multi-element capability.

OP-08**Trace element quantification in crude oils using ICP-QQQ-MS****CHRISTOPH WALKNER¹, REINHARD GRATZER², THOMAS MEISEL¹, SYED NADEEM HUSSEIN BOKHARI¹**¹General and Analytical Chemistry, Montanuniversität Leoben (Austria)²Applied Geosciences and Geophysics, Montanuniversität Leoben (Austria)

Substantial amounts of oil and gas are mined in the Austrian part of the Molasse Basin in the northern Alpine Foreland. Although the organic geochemistry of oils obtained from these sources is already well examined (Gratzer *et al.* 2011), data on trace element contents are scarce. These data could provide additional information on the origin, migration, depositional environment and maturation of oils. Inductively coupled plasma mass spectrometry (ICP-MS) has been widely applied to trace element determination in petroleum samples due to its low detection limits and fast multi-element capability. However, detection of non-metals such as phosphorus and sulphur by quadrupole-based ICP-MS is limited by their high ionization energies and severe polyatomic interferences (Donati *et al.* 2012). The Agilent 8800 triple quadrupole ICP-MS (ICP-QQQ-MS) overcomes these limitations through its high sensitivity and

effective removal of double charged and polyatomic interferences (Balcaen *et al.* 2013). In this contribution we present results for the quantification of trace elements in crude oil samples obtained from various oil fields located in the Austrian part of the Molasse Basin using ICP-QQQ-MS. Prior to analysis, samples were digested in a high pressure asher (HPA-S, Anton Paar) at 300 °C using a HNO₃/H₂O₂-mixture. Therefore external calibration by means of aqueous standards was possible. Mass fractions of 25 elements, ranging over 10 orders of magnitude, were determined. Interferences on the lighter elements were removed by reaction of the target ions with O₂ or NH₃ in the collision/reaction cell of the ICP-QQQ-MS (mass shift mode). The accuracy of the analytical method was confirmed by the analysis of the standard reference materials NIST SRM 1634c (trace elements in fuel oil) and 1084a (wear-metals in lubricating oil).

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OP-09

Influences on the distribution of hydrothermally enriched commodity elements in stream sediments of south west England, investigated using new geochemical baseline survey data.

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The British Geological Survey's Geochemical Baseline Survey of the Environment (G-BASE) has recently completed the collection of 3716 rural stream sediment samples across south west England. High-precision XRF analysis was used to measure the total concentration of 52 major and trace elements in these samples, providing a dataset which captures the stream sediment baseline geochemistry of the region in more detail than ever before.

The application of this data for geochemical mapping provides a visualisation of the spatial distribution of each analysed element in the surface environment across the survey area. Understanding the distribution of a number of elements of interest in stream sediments, which are closely geochemically related to the underlying geology, can be used as a basis to assess targets for mineral exploration and for a variety of environmental applications.

The south west of England is a particularly interesting area in terms of environmental geochemistry: Hydrothermal systems, associated with the emplacement of the granites of the Cornubian batholith in the Permian period have produced an extensive suite of metalliferous mineralisation throughout the study area, which is one of the world's major tin provenances. Since pre-Roman times this

has supported a widespread mining industry, which supplied a wide range of commodity elements; mainly tin (Sn) and copper (Cu), but subordinate lead (Pb), zinc (Zn), arsenic (As), antimony (Sb), iron (Fe), manganese (Mn) and tungsten (W) have also been produced in the past.

This metalliferous mineralisation has resulted in elevated concentrations of these elements in the surface environment of south west England. This is of particular concern, since many of these are recognised as potentially harmful elements (PHEs) which can impact on human, animal, and ecosystem health. Additionally, the legacy of mining and the release of these metals to the environment in mine waste is another potential influence on the observed geochemical baseline of these elements.

We present the results of an investigation into the geological and mineralisation/mining influences on the geochemical baseline for a number of key commodity elements (As, Cu, Pb, Sn, W and Zn) across the area. The spatial extent and distribution of elevated concentrations of the elements enriched in stream sediments due to metalliferous mineralisation are reported and discussed, with reference to the underlying processes and stages of mineralisation which are recognised in the area.

OP-10

Geochemistry of anomalous uranium enrichment in fossil resin

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The radiolytic modification of complex hydrocarbon mixtures proceeds via cleavage, oxidation and aromatization, transforming aliphatic hydrocarbons to aromatic compounds. During radiolysis, water hydroxyl radicals are formed and their reactions lead to increasing degrees of oxidation with the gradual formation of phenols, aromatic ketones, aldehydes and carboxylic acids. Irradiation also causes a decrease in the average size and degree of alkylation of polycyclic aromatic hydrocarbons in the complex mixture of hydrocarbons. The influence of uranium on such structural transformations of the organic fraction of coals and bitumen has been previously reported (Havelcová *et al.* 2014, Kříbek *et al.* 2009), but this paper describes the discovery of a unique fossil resin (amber) containing a high level of uranium that is the cause of the described chemical alterations.

Amber is a term that refers to the fossilized resin of a tree, incorporated into sediments. Fossilization is actually the polymerization of terpenoid compounds that form the general polymeric structure. Because resin is a mixture of compounds, fossil resins are not completely consistent polymers. Moreover, some terpenoids are non-polymerizable, and they stay protected in the fossilized polymer structure. As a result of radiolytic alterations, amber containing high levels of uranium (almost 1.5%) is structurally and chemically significantly different from a fossil resin from the same geological period (Cenomanian, 93.9–100.5 Ma) that does not contain uranium:

- occasional transitions from dark to lighter bands of degraded materials caused by radioactive and thermal alteration were microscopically identified; the sample contained small pores and cracks filled with mineral matter in which the local uranium content reached about 30% w/w, and contained other metals: Zn, Sb, W, Sc, Cr, Fe, Co, Eu, Hf, Ta
- the atomic H/C ratio indicated a decrease in hydrogen during radiolytic degradation and an increased O/C ratio indicated oxidative alteration of the sample amber
- thermogravimetric analysis demonstrated only 52% sample mass loss at a temperature as high as 1050 °C (whereas the sample without uranium was completely destroyed at a temperature of 600 °C), suggesting a higher degree of polymerization of the uranium amber, zonal graphitization, and cross-linking as new C-C bonds were formed in a three-dimensional network
- infrared microspectroscopy showed structural changes of amber in zones with different uranium contents; an increased uranium concentration decreased aliphatic C-bonds and increased C=O functional groups, and total sample aromatization occurred with a uranium content approaching 13% w/w
- gas-chromatographic analysis revealed primarily aromatic hydrocarbons and TMAH-pyrograms were deformed by the unresolved complex mixture as a result of a cross-linked fraction that was not evaporated at the temperature of pyrolysis (610 °C)

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OP-11**Sampling of moisture content in particulate materials****HYLKE GLASS¹**¹ Camborne School of Mines, University of Exeter (UK)

Samples of particulate materials are rarely dry and the moisture content, which may be as high as 20 wt-%, can influence the measured concentrations of chemical properties of interest. The moisture content may change during sample handling or be unrepresentative for the sampled material as a result of a fundamental sampling error. In practice, the variability of moisture content in samples is not always appreciated or well understood. Building on earlier work by Geelhoed and Glass (2004, 2001), this

contribution describes a novel approach to modelling of the variability in the sample moisture content. Following input of key material properties, the model estimates the variance in the sample moisture content. Knowledge of this variance assists in making statistically-sound decisions based on sample analyses. Validation of the model through laboratory experiments suggests that a fundamental error exists which can have a significant effect on sample analyses and their interpretation.

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OP-12**Application of ASTER data in the genesis and Genetic relationship of Barite and Iron Ores in El- Bahariya Oasis Western Desert Egypt****SALEM MOHER¹, AHMED E. KHALIL¹, HATEM M. EL-DESOKY²**¹ Department of Geology, National Research Center, Cairo (Egypt)² Department of Geology, Faculty of Science, Al-Azhar University

The present study aims at exploring the titanite as well as identifying its mineral chemistry and genesis in the basement rocks at Gabal El-Degheimi area. The study area form a part of the Arabian Nubian shield consisting of serpentinite, volcanoclastic metasediments, metagabbro, metavolcanics, older granites, Dokhan volcanics, young granites and alkaline volcanics. The result of Landsat 8 image processing verified by field geology and geochemical

analyses highlighted some alteration zones hosted in the Arc volcanoclastic metasediments as potential source for titanite minerals. They composed of titanite, chlorite, calcite, epidote, sericite, muscovite and biotite in trace amount, about 3wt% of TiO₂ was recorded. Titanite mineral is the main carriers of titanium, calcium and silicon in the volcanoclastic metasediments.

OP-13**Performance comparison of portable XRF instruments: A mineral exploration industry prospective****NIGEL BRAND¹, CHRISTABEL BRAND**¹ Portable XRF Services Pty Ltd, West Perth (Australia)

Within the mineral exploration industry the ability to make an objective assessment and decision on the significance of a sample's chemistry can take days to months through a commercial laboratory by the time a sample is prepared, analysed and results reported. The advancement over the past decade in handheld or portable XRF instruments allows for real time 'fit for purpose' data to be collected allowing for real time assessments and decisions to be made assuming the instruments are used correctly and their limitations understood by the user.

Under standardized test conditions, the analytical performance of portable XRF instruments varies significantly between individual instruments from the same manufacturer, and between manufacturers using similar instruments. The precision of the instruments to repeat a constant element concentration from a single sample is typically very good (<5% RSD); however, the accuracy is generally poor to very poor with large concentration differences in some elements.

Repeat analysis by the same instruments under the same conditions after a two month period shows a

measurable deterioration in element concentration, with elements of lower atomic number, Al and Si, the worst affected. This deterioration in the instruments' performance was observed in all instruments evaluated.

Lithium-ion battery packs, a key to the instruments' portability, can have a measurable effect on the precision and accuracy of the data during a routine battery pack change.

Each instrument provides uniquely individual data that should not be combined with data from any other units without appropriate post-processing or recalibration. To significantly improve the quality and value of the pXRF data, a calibration procedure appropriate to the material(s) being evaluated should be implemented with regular baseline data collected to ensure instrument and data stability.

Over time, matrix calibrations need to be verified with the instrument undergoing a manufacturer's recalibration when control limits deteriorate significantly.

OP-14**Calibration strategies for geo-environmental XRF analysis****MARK INGHAM¹**¹ Environmental Science Centre, Nottingham (UK)

With more and more emphasis being put on the traceability of results what are the strategies available for the calibration of X-ray Fluorescence Spectrometers to be used for geo-environmental

analysis. The use and applicability of both synthetic standards and natural reference materials will be discussed.

OP-15**Problems with elements not included in the software of handheld XRF analysers****ALESSANDRA RACHETTI¹, KRISTINA STOCKER, WOLFHARD WEGSCHEIDER, JOHANN G RAITH**¹ General and Analytical Chemistry, Montanuniversität Leoben (Austria)

Small portable XRF analysers are widely used for prospecting in the mining industry and plenty commercial applications are explicitly advertised by the manufacturers. Unfortunately the analyst is depending on the software to include all potentially interfering elements.

In this work we explore the effect of a neglected element, yttrium, on the quantification of the element of interest, niobium, in the analysis of stream sediments and granite eluvium of different concentrates. The samples stem from the Bohemian Massif (Austria) and are investigated in order to verify known geochemical anomalies and their potential use as prospectivity indicators for coltan deposits within this area.

The first strategy to account for yttrium not in calibration was to fit the spectra with the freely available software PyMca [<http://pymca.sourceforge>].

net/] and to use the resulting net intensities of the element peaks for a multivariate calibration. Correct concentrations for yttrium and other elements were supplied by independent ICP MS analyses. Advantages and limitations of this approach will be discussed. This approach was favoured as samples representing intermediary steps of preparation were not available for a second measurement anyway.

The second strategy was to send the instrument back to the manufacturer and ask for a recalibration including the missing element. This was rated second best as the remeasurement of 700 + samples was either not possible and/or tedious affair. Good thing that the manufacturer showed consideration for time lost and did the software update for free.

Data from before and after recalibration and the data from the multivariate approach will be compared.

OP-16**Analysis of rare earth elements in soils and sediments****SEBASTIAN WÜNSCHER¹, RENÉ CHEMNITZER¹**¹ Analytik Jena AG, Jena (Germany)

The applications for trace elemental analysis are steadily increasing: beside the classical fields such as environmental, geochemical and semiconductor analysis more and more interest for trace elemental analysis in food and material characterization can be observed, not to forget hot topics such as analysis of isotope ratios and nanoparticles.

ICP-MS, as high sensitive analytical technique, is widely used to characterize a variety of sample types. However, trace element analysis in the presence of high matrix loadings remains challenging due to high factors of dilution that are required in order to compensate for the disadvantages of high matrix concentrations.

For the reliable detection of trace elements like rare earth elements, high sensitivity is key in ICP-MS.

Furthermore, analyzing samples containing both, concentrated analytes in the ppm to percent range and elements in trace concentrations (sub ppb to ppt) requires a wide detector range and low abundance sensitivity.

In this regard, the Analytik Jena PlasmaQuant® MS Elite comprises many of the technical prerequisites in order to fulfill all requirements for the characterization of trace elements in geological samples. Its unconventional ion optics design results in an outstanding sensitivity of 1.5 GHz/ppm while keeping the oxide formation below 2%.

The presentation will describe the use of the high sensitivity PlasmaQuant® MS Elite in the field of trace element analysis of rare earth elements in geological samples.

OP-17

Removal of Interferences on platinum in Platinum Group Elements (PGE) reference materials (RM)

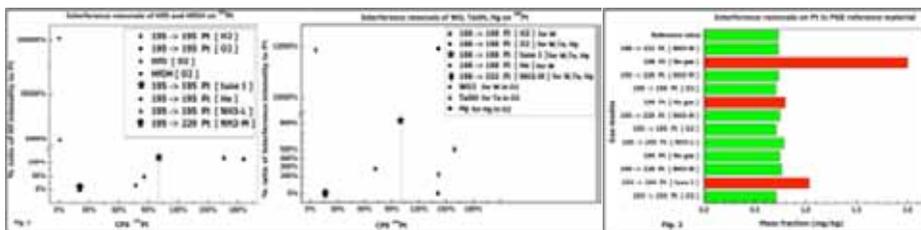
SYED NADEEM HUSSAIN BOKHARI ¹, THOMAS MEISEL ¹, CHRISTOPH WALKNER¹ General and Analytical Chemistry, Montanuniversität Leoben (Austria)

Platinum group elements (PGE) are essential industrial metals with high world demand due to their unique properties. PGE supply chain is being fulfilled from alternate sources e.g. recycling from industrial wastes, electronics and catalytic converter as well as from natural exploration. Platinum is one of the important elements in ICP-MS spectrum which suffer from severe interferences in complex matrices. Expected interferences on platinum isotopes are ^{178,179,180}Hf¹⁶O, ^{178,179}Hf¹⁶O¹H, ^{154,155,156,158}Gd⁴⁰Ar, ¹⁵⁴Sm⁴⁰Ar, ^{180,182}W¹⁶O, ¹⁸¹Ta¹⁶O¹H and ^{196,198}Hg.

The ICP-MS/MS Agilent 8800 can remove interferences in reaction collision cell with mass shifts and different gases. We aim to remove interferences on Pt (for direct and isotope dilution analysis) instead of chemical separations. Initial tests were performed on pure solutions of 1 mg/l (interfering elements): 1 ng/l (Pt) respectively. Outcomes of initial tests were applied to PGE reference materials WMG-1, SARM-7

and PTC-1 (digested with Na₂O₂ sintering).

The results with pure solutions indicate ^{178,179,180}Hf¹⁶O have severe interferences on ^{194,195,196}Pt isotopes and ^{178,179}Hf¹⁶O¹H interfere ^{195,196}Pt. GdAr, SmAr interferences are minor. ¹⁸¹Ta¹⁶O¹H produce severe interference on ¹⁹⁸Pt, ^{180,182}W¹⁶O and ^{196,198}Hg has severe interferences on ^{196,198}Pt. These interferences can be best removed by the formation of Pt(NH₃)₂ complexes [1] and on-mass measurement in NH₃ gas for Hf as shown in fig. 1. ^{180,182}WO⁺ interferences on ^{196,198}Pt can be removed with O₂ as tungsten tends to form oxides stable WO₂ and WO₃ in stream of oxygen [2]. However samples with substantial amounts of Ta, Hf and Hg tend to form MO⁺, MOH⁺ and MH⁺ in O₂ and H₂ gases. Therefore Pt(NH₃)₂ is best compromise inspite of low intensities. The results obtained comply with certified values as in fig. 2. The developed method is being tested on low concentration PGE reference materials.



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OP-18

Principles of LA-QQQ-ICP-MS and opportunities in Earth Sciences

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Dynamic reaction cells (DRS) have been proven to be a useful addition to routine quadrupole-ICP-MS analysis for more than a decade in reducing problems caused by polyatomic interferences. Placed in front of the quadrupole, the DRS can however produce new, unwanted interferences when analyzing complex samples. Sandwiching a DRS in-between two quadrupoles efficiently eliminates those unwanted interferences. This concept has been implemented in the Agilent 8800QQQ, of which one of the first machines coupled to a laser ablation system in Earth Sciences, had been installed in Gothenburg in 2014.

One quadrupole placed before the DRS allows entrance only of ions with m/z identical to the ion of interest. A wide range of reactive gases can circulate through the DRS and interact with incoming ions. Such gas phase reactions with cations can be highly selective, forming several classes of product ions. The second quadrupole is able to selectively filter out those different product ions. Operating the ICP-MS in such a manner is called MS/MS mode, to distinguish it from operation with only a single quadrupole active (called SQ mode).

In principle, performing routine analysis in MS/MS mode with sample introduction by laser ablation (LA) is fundamentally different compared with typical sample introduction in solution. On the one hand, time-resolved transient laser ablation signals have to be gathered using only one reactive gas, while solutions can be introduced under constant conditions for several minutes, hence allowing switching between several reactive gases. On the other hand, because of the dry nature and hotter

plasma, sample introduction by laser ablation causes a more restrictive and simpler range of polyatomic interferences (primarily diatomic ions with metals and C, N, O and Ar) compared to solution introduction.

We have performed systematic studies on trace element determination of several important minerals (e.g., quartz, magnetite, apatite) using the reactive gases H₂, O₂ and NH₃ and compared the results with SQ mode. As expected, dramatic improvements in detection limits could be derived for several elements (e.g., factor 500 for Se in O₂ mode, factor 5 for Fe in O₂ and H₂ mode, factor 4 for Cl in H₂ mode). However, the most important finding here is that precision and accuracy were not significantly reduced for most of the other elements. This opens up the opportunity to set up one protocol only for each mineral of interest without the need to analyse the same area several times with different modes. For example, the O₂ mode has been implemented for magnetite analysis, while halogens in apatite are run in H₂ mode.

Potentially even more significant is the finding that several isobaric interferences can be separated from each other with surprising efficiency. In particular, we are able to separate ¹⁷⁶Hf from ¹⁷⁶Yb and ¹⁷⁶Lu without losing sensitivity, allowing in-situ Lu/Hf dating of Lu-rich minerals such as xenotime. Although with reduced sensitivity, we are also able to separate ⁸⁷Sr from ⁸⁷Rb, allowing in-situ Rb/Sr dating of Rb-rich minerals such as biotite. It has to be stressed that %-level precisions are more than sufficient to allow geologically meaningful dating if daughter isotopes can both be measured interference free in minerals with high concentrations in mother isotopes.

OP-19

Radiogenic and stable isotope study of the Vologochan and Mikchangda ore-bearing intrusions of the Noril'sk Province: Implications for exploration

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Despite the long-term study of the world-class Ni-Cu-PGE sulfide deposits related to the Kharaelakh, Talnakh and Noril'sk-1 mafic-ultramafic intrusions within the Noril'sk Province they remain a subject of ongoing debate related to their origin. Understanding the processes behind the formation of economically important ore deposits is crucial for locating additional deposits in areas that have not been previously considered. This study, therefore, aimed to provide isotope-geochemical fingerprinting to be used in exploration for Ni-Cu-PGE sulfide ores.

We present Hf-Nd-Cu-S isotope data for the same suite of lithologies and associated disseminated Ni-Cu-PGE sulfide ores from the subeconomic Vologochan and prospective Mikchangda intrusions of the Noril'sk Province. The rocks investigated comprise sulfide-rich varieties of olivine gabbro and melanocratic troctolite occurring in bottom parts of the intrusions. In situ Hf isotope data were collected on the dated spots within single zircon grains. The analysis used a New Wave LUV213 laser-ablation microprobe attached to a Nu plasma MC-ICP-MS at GEMOC. Details of Nd- and Cu-S isotope analyses performed at the Russian Geological Research Institute (St. Petersburg, Russia) are outlined in Malitch *et al.* (2013; 2014).

Zircons from the Vologochan and Mikchangda intrusions yielded broadly similar $\epsilon_{\text{Hf}}(T)$ (parts in 10^4 difference between the zircon sample and the

chondritic reservoir) values from +6.5 to +18.7 (mean ϵ_{Hf} +9.8, $n=12$) at Vologochan and from +8.1 to +12.7 (mean ϵ_{Hf} +10.9, $n=7$) at Mikchangda; both are close to the mean value of the depleted mantle reservoir at that time. Similarly, in terms of Cu-isotopes, the majority of the analyzed sulfide samples fall within a tight cluster of $\delta^{65}\text{Cu}$ values (from -1.4 to -0.2‰, with a mean of -0.7‰ and a standard deviation of 0.15‰ at Vologochan, and from -1.1 to -0.3‰ and a mean of -0.8 ± 0.2 ‰ at Mikchangda), characteristic of the ores from the economic Ni-Cu-PGE deposits at Talnakh and Stillwater (Malitch *et al.* 2014). In contrast, lithologies and disseminated ores at Vologochan and Mikchangda show distinct Nd-S isotope signatures ($\epsilon_{\text{Nd}}=1.2 \pm 0.2$ and $\delta^{34}\text{S}=7.0 \pm 0.3$ ‰ at Vologochan, $\epsilon_{\text{Nd}}=2.4 \pm 0.2$ and $\delta^{34}\text{S}=12.8 \pm 0.6$ ‰ at Mikchangda).

Hf-S-Cu isotope parameters of rocks and sulfide ores from the Mikchangda intrusion closely match those from the economic Talnakh intrusion and may be considered as most promising in targeting the massive Ni-Cu-PGE sulfide ores. Integrated radiogenic and stable isotope data can be employed as a useful indicator of the potential for hosting Ni-Cu-PGE sulfide deposits.

The study was supported by RFBR (grant 13-05-00671-a).

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OP-20

Application of luminescence dating and lead isotope analysis to authenticate and provenance a bronze artefact from northern Australia

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A bronze cannon purported to be found on a Northern Territory beach southwest of Darwin in 2010 was thought by museum authorities to possibly be a modern reproduction of a sixteenth century Portuguese weapon. Archaeological surveys have failed to locate any associated relics and there are no known Portuguese or later shipwrecks in the vicinity of the find. Metallurgical, dating and stylistic analyses are being utilized to authenticate and provenance the gun. These include optically stimulated luminescence (OSL) and accelerator mass spectrometry (AMS) radiocarbon dating methods applied to sediment in the gun to assess how long it might have been encased in the barrel. The OSL results suggest that most of the sand in the barrel was last exposed to sunlight around 250 years ago, strongly discounting

the notion that the gun is a modern reproduction. Although younger sand is present and an AMS radiocarbon age from seaweed in the barrel gave an age after AD 1950, these are probably more recent contaminants. Lead isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb were measured by MC-ICP-MS on two samples of bronze from the gun. Of known historical lead sources, the lead isotopic signature is most similar to that of several ores from the Iberian Peninsula. However, lead is widely recycled and stylistically the gun is most likely an Indonesian reproduction of European original. It has been theorized that eighteenth century Macassans involved in the trepang trade or perhaps a slaving party of Balinese or Banda islanders may have lost the gun.

OP-21 ABSOLUTE CALIBRATION FOR THE EMPA-FT

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The Fission-Track Thermochronology (FTT) has been applied for decades to quantify rates and timing of processes in the shallow crust. The most widely used approach is the External Detector Method (EDM). The surface density of fossil fission tracks gives the information on the time ²³⁸U spontaneous fission is being registered, and therefore the fission-track age, provided that the uranium concentration can be determined. In EDM, this determination is carried out by inducing fission in the ²³⁵U with neutrons in a nuclear reactor and counting the resulting tracks. Based on the studies made by Gombosi *et al.*, (2014), we present an alternative method of dating zircons using an electron probe microanalysis (EMPA) to measure uranium concentration [U]. The electron microprobe analyzer fission-track (EMPA-FT) method was applied to three samples of rapidly cooled zircons: the Fish Canyon Tuff, Poços de Caldas (syenite) and Serra Geral zircons. The analyses were made using two approaches: 1) using the age equation described in Gombosi *et al.* (2014) and 2) using a new age equation, based on the absolute calibration, developed for this work. The results using Gombosi's age equation were 26.7 ± 4.1, 80.6 ± 12.8 and 130.9 ± 20.1, respectively and the results using this work age equation were 27.8 ± 1.9, 83.8 ± 7.7 and 136 ± 12, respectively. The uncertainty of the age of is affected mainly by components that N₂₃₈ (²³⁸U quantity) and S (spontaneous fission-track density). Other factors can affect the uncertainty of

the age, but their contributions are very small. As in Gombosi *et al.*, (2014), the uncertainty on the single grain age is assumed to be a Poisson distribution. Despite this, note that the results are consistent with each other and all samples yield ages that overlap within two standard deviations of published reference ages determined from radiometric techniques (i.e., K/Ar, ⁴⁰Ar/³⁹Ar, and U/Pb) and the traditional FTT by EDM. The EPMA-FT technique avoids the hazards of thermal neutron irradiation and allows simultaneous chemical compositions to be determined, but presents a disadvantage in comparison with the EDM: the samples dated by EPMA-FT must have a high Uranium concentrations (> 50 ppm). In lower concentrations, the EDM is more sensitive. However, the EMPA-FT method overcomes challenges associated with the LA-ICP-MS technique: i) Non-destructive technique; ii) smaller spot (5µm) than LA-ICP-MS (20 – 50 µm). This virtually eliminates the concern with precise alignment associated with zoning in zircon (regions with lower ages than the core - metamorphism indicators); and iii) greater accuracy in tracking of actinides (i.e., U, Th) that are associated with radiation damage and the zircon behavior against annealing - this may allow a better understanding the relationship between annealing and composition and/or radiation damage. Therefore, in many geologic applications EPMA-FT may be an advantageous technique due to its low cost, fast turnaround time, and the avoidance of neutron irradiation.

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OP-22 Careful validation of U-Th zircon dating by LA- ICP-MS

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Zircon crystals in the age range of ca. 1 to 300 ka can be dated by ²³⁰Th/²³⁸U disequilibrium methods because of the strong fractionation between Th and U during crystallization of zircon from melts. LA-ICP-MS analysis of eight commonly used secular equilibrium reference zircons and synthetic zircon indicate that corrections for abundance sensitivity and dizirconiumtrioxid molecular ions (Zr₂O₃⁺) are critical for reliable determination of ²³⁰Th abundances in zircon. When corrected for abundance sensitivity and interferences, activity ratios of (²³⁰Th)/(²³⁸U) for the eight reference zircons analyzed average 1.001±0.010 (1 error; mean square of weighted deviates MSWD = 1.45; n = 8), consistent with their old Pb/U ages that imply equilibrium for all intermediate daughter isotopes (including ²³⁰Th) within the ²³⁸U decay chain. Uranium series zircon ages generated by LA-ICP-MS

without mitigating (e.g., by high mass resolution) or correcting for abundance sensitivity and molecular interferences on ²³⁰Th are potentially unreliable. To validate the applicability of LA-ICP-MS to this dating method, we also acquired data for three late Quaternary volcanic rocks; the 161 ka Kos Plateau Tuff, the 12 ka Puy de Dôme trachyte lava, and the 40 ka Campanian ignimbrite (all ages are independently determined eruption ages with zircon being of equal or slightly older age). A comparison of the corrected LA-ICP-MS results with previously published SIMS and TIMS data for these rocks shows concordant ages with equivalent precision for LA- ICP-MS and SIMS, but much much briefer (by approximately one order-of-magnitude) analysis durations per spot for LA-ICP-MS compared to SIMS.

OP-23 Performance Capabilities of the Cameca 1280-HR SIMS Instrument

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Since December 2013 the Helmholtz Zentrum Potsdam has operated a 1280-HR instrument: the latest generation of Cameca large geometry ion microprobe. Here we report the observed performance of this tool, with particular emphasis on the determination of isotopic ratios on geomaterials.

We have already acquired extensive experience in the determination of $\delta^{18}\text{O}$ values in silicates, for which a single analysis requires circa 80 seconds of actual data acquisition. Running in full automatic mode and with the reference material(s) embedded within the grain mount, we are thus able to complete some 250 analyses in a 24 hour cycle. For such analyses we typically achieve an analytical repeatability of ± 0.15 ‰ (1sd), though we have recorded repeatabilities down to ± 0.092 ‰ (1sd, $n = 100$) in one suite of zircon analyses. A main consideration in $\delta^{18}\text{O}$ analyses with the 1280-HR is the need for careful sample preparation: on samples with as little as 5 μm topographic relief between silicate grains and epoxy embedding media we have observed charging problems despite using both a 35 nm gold coating and $> 1 \mu\text{A}$ of low energy electron flooding.

Thanks to the availability of a well characterized suite of tourmaline RMs, boron isotope analyses are already a well established application in the Potsdam SIMS facility. Here a single analysis involves 80 s of data acquisition, from which we can obtain a typical repeatability of ± 0.25 ‰ (1sd) and an overall analytical uncertainty of ± 0.9 ‰ based on a suite of four distinct tourmaline RMs. We have also been

able to analyze the boron isotopic compositions on areas as small as 3 μm with only a modest reduction in overall precision.

Large demand exists for U-Th-Pb age determinations, for which we currently have RMs only for zircon. For such work a single analysis commonly requires 12 to 15 minutes of data acquisition, meaning that a complete project typically involves *circa* 5 days of laboratory usage. Our zircon U-Pb protocol calls for the analysis of a quality control material during all analytical sessions. Here we often observe a ~ 1 % bias in the Pb/U results from the QCM as calibrated by the primary reference material. We conclude that under normal circumstances our inter-element results are reliable at the ± 2 ‰ level. A key feature of the 1280-HR tool is the ability to conduct oxygen flooding during the analyses, which results in a 2x improvement in instrument sensitivity for Pb data acquisition.

The technology behind the 1280-HR is sufficiently mature such that the main factor limiting analytical quality has, at least in some isotopic systems, become the interlaboratory bias observed during the "bulk" characterization of the reference materials. A key limiting factor in the performance of the instrument itself is the constraint that only a single, 1-inch diameter sample may be in the secondary ion source at a time. This limitation often compels frequent sample exchanges in order to access calibration materials, thereby prohibiting extended automated runs.

OP-24 What role can and should play ion beam analytical methods in the context of geometallurgy?

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Geochemical analysis in the domain of the value-added chain of mineral raw materials is designed to support purposeful the development and improvement of technologies.

Linking chemical and mineralogical data as well as information about the microstructure of ores and gangue minerals with general and specific models of the respective deposits allows the establishment of efficient input data for a targeted impact on mineral processing and metallurgical technologies. These interrelations describe the scientific subfield of geomettallurgy. Classical exploration geochemistry and analytical methods for process control are added among it.

This relevancy to technologies and process control implicates specific requirements on the analytical methods regarding accuracy, precision, traceability, but also on availability, response time and sample throughput.

Ion beam analysis (IBA) has a well-earned reputation of an elaborate and complex analytical method, which is furthermore, difficult and strongly regulated

to access. In addition is the treatment of the data ambitious and poorly automatable.

What role can and should IBA play in the context of geomettallurgy and process control?

We will answer this question on a selection of examples and methods used and developed at the Helmholtz-Institute Freiberg in close cooperation with the Ion Beam Center of the Helmholtz-Zentrum Dresden-Rossendorf. In detail we will show:

- 1.) the application of the High-Speed PIXE (particle induced X-ray emission) to determine the lateral distribution of trace elements in large samples like drill cores or rock-chips,
- 2.) the chemical composition (H – U) of reference materials for microanalytical methods using a combination of PIXE, particle induced gamma emission (PIGE), nuclear reaction analysis (NRA) and Rutherford backscattering spectroscopy (RBS) and
- 3.) the validation and support of proof of concept and proof of performance procedures of new process analytical methods.

OP-25

Particle size matters: A new strategy for manufacturing microanalytical reference standards from nano-particulate powder pellets

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The backbone of reliable measurements are reference standards that are used for both the calibration and validation of geochemical, in situ micro-analytical data. Standards should match the unknown sample compositions as closely as possible in their physical and chemical properties and must be homogeneous down to micrometer sampling at sub-ppm concentration levels and isotopic composition. Natural or synthesized minerals that are homogeneous enough for this purpose are extremely rare. Widely used are glasses manufactured from melted natural geological standards (e.g., USGS BHVO-2G, BIR-1G; Jochum *et al.* 2005; MPI-DING glasses: Jochum *et al.* 2006). But, not all geological materials can be vitrified without addition of a flux, and vitrification bears the risk of losing volatile components. Homogeneity of pulverized materials is a function of both sampled volume and grain size. For most materials the availability of well-characterized standards ready for micro-analysis that combine these properties is rather limited. However, well-characterized powder standards are available in large number and variety, or can be synthesized and subsequently pressed into pellets.

Nano-particulate pressed powder tablets ("nano-pellets") are highly cohesive and can be manufactured without addition of any binding agent. They are

suitable for e.g., LA-ICP-MS and EPMA in situ micro analysis. We prepared nano-particulate powders with grain size of less than $d_{50}=100-400\text{nm}$ (Fig.1) using a high-power planetary ball mill and wet milling protocols in aqueous suspension (Garbe-Schönberg and Müller 2014). In this way homogeneity increases to a level that enables high precision measurements of elemental composition by LA-ICP-MS with RSD 1-5% with high spatial resolution (spot size 10-32 μm diameter) (Figs.2 & 3). First data on Li and B isotopic composition is reported by (Le Roux *et al.* 2015) during this conference. This technique also accomplishes the mixing of different solid materials for e.g., elemental and isotopic spiking and concentration series of calibration standards. So far, we manufactured "nano-pellets" from biogenic carbonate standards JCp-1 and Jct-1 (GSJ) that are currently studied with an international laboratory inter-comparison run; from a selection of USGS rock powders (BIR-1, BHVO-2, MRG-1 etc.) and synthetic standards (MACS-3, MAPS-4, -5, MASS-1); from Fe,Mn-oxihydroxides (IF-G, FER-1, FER-2: Sampaio and Enzweiler 2014; NOD-P1, NOD-A1 etc.); from IAG standards OKUM and MUH-1 (Meisel Th. pers. comm.); and from San Carlos olivine (SCO). We are currently seeking labs that are interested in the characterization of manufactured "nano-pellet" geostandards.

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OP-26

Development of the matrix-matched sphalerite (ZnS) standards MUL-ZnS-1 and MUL-ZnS-2 for in-situ analysis of trace elements by laser ablation inductively coupled plasma-mass spectroscopy (LA-ICP-MS)

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Sphalerite (ZnS) is an abundant ore mineral and an important carrier of critical high-technology elements such as Ge, Ga and In. These trace elements were defined by the "Ad-Hoc Working Group on defining critical raw materials" of the European Union (EU) as being critical and are used in high-technology products such as electronics and green technologies (EU 2014). In-situ analysis of trace elements in natural sphalerite samples using LA-ICP-MS is hampered by a lack of availability of suitable homogenous matrix-matched sulfide calibration standards. The necessity of matrix matched standards is discussed by many authors, e.g. Kuhn and Günther (2003), Ballhaus *et al.* (2006). The use of natural sphalerite samples as standard reference material is the ideal case, but homogenous sphalerite minerals with a wide range of trace elements are extremely rare in ore deposits (Cook *et al.* 2009, Cerny 1989). The synthesis of the standards MUL-ZnS1 and MUL-ZnS2 by incorporating 17 trace elements in two different (Zn,Fe)S matrices is reported here. As raw material for the (Fe,Zn)S matrix zinc sulphide purum

$\geq 97.0\%$ (nanocrystal powder) with $D_{50} < 0.5\mu\text{m}$ and iron(II) sulphide technical grade are used. For the trace elements cadmium sulphide 98% (Cd), silver (I) selenide (Ag, Se), natural stibnite (Sb) and galena (Pb) were mixed with ultrapure water and ground in a Pulverisette 7 planetary mill (7 cycles, 15min grinding, 30min break for cooling). The trace elements As, Cu, Mo, Cr, Co, Ti, Ge, Ga, Mn, Bi, In and Ni were doped as single element ICP-MS standard solutions. The powder was pressed at a pressure of 10 tons to pellets with a diameter of 32mm and sintered at 400°C for 100 hours using Argon as inert gas. To confirm the homogeneity of major and trace element distributions, chemical analyses were performed using EMPA and LA-ICP-MS for in-situ analysis. To quantify the element content several High Pressure Asher (HPA) digestions of different sintered pellets were prepared and analyzed as solutions using (QQ) ICP-MS, and ICP-OES. The results indicate that the two standards are homogenous calibration standards for LA-ICP-MS analysis of most trace elements in sphalerite.

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OP-27

Characterizing isotopic homogeneity of candidate reference materials at the picogram sampling scale

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Modern in situ analytical methods can determine isotopic ratios in solid materials with sampling masses in the low nanogram (LA-ICPMS) to mid-picogram (SIMS) mass ranges with repeatabilities at, or even below ± 0.1 ‰ (1sd). The proper use of such analytical technologies is, however, constrained by a near total absence of geological RMs that have been adequately characterized for their heterogeneity at such small sampling scales. In many cases the heterogeneity component determined at the “bulk” scale (micrograms to milligrams) is assumed to be valid at the smaller sampling scale, often in the absence of any rigorous in situ testing. Those characterizations that have evaluated the fine scale heterogeneity of a candidate RM have often resorted to comparing the observed repeatability to that presumed for the given analytical method. In the cases where these two values are similar it has been asserted that a given material is “homogeneous” at the micrometer scale.

Our research applies statistical methods to SIMS data for quantifying isotopic heterogeneity at the sub-picogram sampling scale, meaning that the analytical uncertainty intrinsic to our laboratory method must be quantified using analysis of variance (ANOVA) and then subtracted during data evaluation. Our work

has focused on developing a metrologically rigorous RM for $\delta^{18}\text{O}$ in quartz, for which suitable materials already exist at the bulk sampling scale. Our Cameca 1280-HR SIMS instrument has been able to provide an analytical repeatability down to ± 0.092 ‰ (1sd, $n = 100$) on silicates. Hence, the uncertainty for the $\delta^{18}\text{O}$ value of the RM, including its heterogeneity component, should be known at significantly better than this level. Only under such conditions can the full capability of this technology be exploited in a metrologically rigorous fashion.

A second objective of our work is to develop a strategy for predicting sample heterogeneity at larger sampling masses based on data obtained at the picogram sampling scale. We utilize the modelling of the newly defined ‘heterogeneity factor’ as a function of scale, as previously established with elemental measurements at the macroscopic measurement scale (Ramsey *et al.* 2013). Here we make use of not only the $^{18}\text{O}/^{16}\text{O}$ - ratios observed by SIMS, but also the grain size distribution of the material being tested. This second component is important in order to understand the risks involved when only a single or small number of grains/fragments of an RM can be used for calibrating an analytical series.

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OP-28

The search for suitable reference materials for microanalytical analyses of Mn rich samples

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Since over 200 years a number of studies have debated the origin of the black or brown, up to 250 μm thick manganese-rich coatings on rocks, referred to as rock varnish. A great amount of literature about this material has been published, but no suitable or consistent reference materials (RMs) have been established to calibrate analytical data from microanalytical techniques. We have therefore investigated a number of RMs [FeMn-1 (IAG), NOD P-1 (USGS) and JMn-1 (GSJ) from the Pacific Ocean and NODA-1 (USGS) from the Atlantic Ocean] whether they fit the requirements for an appropriate RM for Mn- rich samples. We pressed the powdered Mn nodule RMs (4 t, 15 min, evacuated press, resin and additive free) to produce pellets suitable for laser ablation ICP-MS. Furthermore, the synthetic NISTSRM 610 silicate glass with its high trace element contents and the GSE-1G (USGS) basaltic glass with its geologic composition were investigated. Up to now, the well-known NISTSRM 61X glasses and the GSE-1G basaltic glass were used for the calibration of the Mn-rich materials (Wayne *et al.* 2006, Nowinski *et al.* 2010, Macholdt *et al.* 2015); however, these samples suffer from low Mn and/or Fe contents. Investigations were performed using a combination of a ThermoFisher Element2 single-collector sector- field ICP-MS and an Electro Scientific Industries (ESI) femtosecond laser ablation system, NWR-Femto, operating a wavelength of 200 nm, and producing laser pulses at 150 fs. For comparison, a New Wave UP213 Nd:YAG laser ablation system

with a wavelength of 213 nm was also coupled to the Element2 ICP-MS, producing laser pulses of 5 ns. Operating parameters, such as spot size (8-40 μm), line scan speed (1-5 $\mu\text{m s}^{-1}$), pulse repetition rate (5-125 Hz) and energy density (0.1-9.2 J cm^{-2}) were adjusted to determine reproducibility, measurement accuracy, mass load induced matrix and element fractionation effects, specifically for selected volatile, chalcophile and siderophile elements of the RMs. Our preliminary results demonstrate that the sensitivity factors are independent of the tested crater size and energy density ranges. Ratios of highly abundant elements in Mn-rich samples, such as Fe/Mn, can be reliably determined with small crater sizes (8 μm) and low energy densities (0.1 J cm^{-1}) (Jochum *et al.* Goldschmidt conference 2015). A possible disadvantage of the pressed powder pellets, compared to the glass RMs, is the inhomogeneity for some elements for test portions of a few hundred picograms consumed by fs LA-ICP-MS microanalyses. In summary, the four nodules materials have the advantage of a matrix-matched calibration, especially for ns laser ablation with its possible element fractionation and mass-load-induced matrix effects. However, the disadvantage of the Mn-rich RMs is the heterogeneity of some elements for small test portions of ablated material. Therefore, the choice of the right RM for microanalytical analyses of Mn-rich materials is mostly dependent on the analytical challenge that needs to be met.

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OP-29

Comparison of ablation of different sulphides as a function of the type of nano-second pulse width laser ablation system

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Elemental fractionation (non-stoichiometric effects) during LA-ICP-MS analysis occurs during sample ablation, aerosol formation, sample transport, and vaporization, atomisation and ionisation within the ICP. In addition to being matrix dependent (e.g. Gunther *et al.* 2005), those processes also depend on the wavelengths and pulse widths of laser systems (e.g. Guillong *et al.* 2005). Some element fractionation could also occur during aerosol transport (e.g. Loewen *et al.* 2012) implying that cell design is also an important factor in LA-ICPMS analysis. For sulphide analysis laser fluence (J/cm²) is also important as melting can occur at the ablation site especially at high fluence (Gilbert *et al.* 2014). Ablation of different sulphide minerals results in variable amounts of fractionation between metals and sulphur (Gilbert *et al.* 2014), and also between volatile and refractory metals e.g., Zn, Cd, W relative to Fe (Danyushevsky *et al.* 2011). In this study we have compared elemental fractionation during ablation of several powdered sulphide mixes and the new calibration standard STDGL-3 using several different nano-second pulse width laser ablation systems.

A new calibration standard for LA-ICP-MS analysis of sulphide minerals STDGL-3 was developed due to inhomogeneous distribution of some elements in previously available standards i.e., STDGL2b2 (Danyushevsky *et al.* 2011) and MASS-1 (Wilson *et al.* 2002). Lithium-borate based glasses with dissolved sulphides have been shown to be a better matrix match for quantification of sulphides analyses than silicate glasses (e.g. NIST glasses) and more homogeneous and stable than powdered sulphides (Danyushevsky *et al.* 2011). We have used a Li-borate based flux doped with a wide range of chalcophile and siderophile elements, and elements required for assessing common interferences (e.g., Gd, Hf, Ta, W, Zr, Sr). The doped flux was mixed with Fe- and Zn-rich sulphide powders (i.e., CZN-3 and RTS-4) and fused to produce a homogeneous glass. A preparation procedure was developed to ensure efficient mixing while retaining volatile elements (Se, Tl) and preventing formation of Au and Pt micro inclusions. The glass produced is characterised by improved homogeneity: RSDs for most elements are below 3%, below 5% for Au and Pt, and below 7% for Se using 50 µm spot sizes.

To assess differences in elemental fractionation during the analysis of different sulphides using laser systems with different wavelengths, finely ground sulphide mixes (<5 micron) were prepared and pressed into solid pellets. We have analysed these sulphide mixed with two excimer lasers with 193 and 248 nm wavelengths and the same sample chamber design, and compared these results with a 213 nm Nd:YAG

laser system which has a different sample chamber design. All laser systems were coupled with an Agilent 7700 ICPMS. The matrix effects between different sulphides and STDGL-3 are also assessed with the laser systems mentioned above. Correction factors allowing for accurate measurements of trace element concentrations in sulphide minerals when using STDGL-3 as a calibration standard are calculated.

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OP-30

Revisiting the chromium reference value in BRP-1 (Basalt Ribeirão Preto)

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The production of geochemical reference materials (RM) in Brazil is mostly intended to supply the needs of the mineral industry. In an isolated effort to produce RM for geochemical applications, some Brazilian institutions assisted by the USGS and the IAG, produced the certified reference material called BRP-1, Basalt Ribeirão Preto (Cotta and Enzweiler 2008). The rock sample was collected, comminuted, split and characterized following international recommendations, such as the IAG protocol for the production of RM (Kane *et al.* 2003), which is based on experience of the geological community plus ISO guidelines. Mostly, BRP-1 was mostly characterized by a set of laboratories that accepted an invitation based on acceptable performance during the analysis of another basalt in a GeoPT proficiency test. The certificate of BRP-1 reports reference values (RV) for 44 constituents and 13 informational values.

During the characterization step, together with two units of BRP-1, each laboratory received a portion of USGS BCR-2 (Basalt Columbia River) reference material as a blind quality control sample. The results reported by the laboratories for BCR-2 compared with its recommended value within $RV \pm 2s$ (s = standard deviation of the RV) were used as a filter for acceptance of laboratory data for inclusion in the data set to calculate the RV for BRP-1. This procedure was successful for most constituents, but analytical results

acquired after the certification of BRP-1 tended to be lower than the Cr reference values of BRP-1 (12.4 ± 1.0 mg.kg⁻¹) and BCR-2 (18 ± 2 mg.kg⁻¹).

Examples are ID-ICP-MS published results (BCR-2 = 16.5 ± 0.3 and BRP-1 = 10.7 ± 0.2 mg.kg⁻¹) (Cotta and Enzweiler 2013), and external calibration ICP-MS values (BCR-2 = 16 ± 1 and BRP-1 = 11.4 ± 0.7 mg.kg⁻¹) (Cotta and Enzweiler 2012). Additionally, BRP-1 was the test sample of GeoPT25, where 63 laboratories provided data for Cr with a resultant assigned a provisional value of 10.7 ± 0.5 mg.kg⁻¹ (Webb *et al.* 2009). And in a new evaluation of published data for the most used geochemical RM, Jochum *et al.* (2015) proposed 15.88 ± 0.41 mg.kg⁻¹ as reference value for Cr in BCR-2. From the above we infer that the positive bias associated to the Cr value in BCR-2 was transferred to BRP-1.

After a re-evaluation of the original data, we propose a revised RV for Cr in BRP-1 of 11.0 ± 0.9 mg.kg⁻¹. For the new calculation, we added ID-ICP-MS results to the dataset and the BCR-2 reported values were not anymore a data exclusion criterion. The larger number of used datasets (15 against 11 in the original certification) and the little smaller uncertainty of the new RV suggest that this is a more robust estimation of the Cr value in BRP-1.

OP-31

BPbISO-1G, a synthetic geologic glass designed to facilitate lead isotopic analysis in geologic materials

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With the increased interest in microanalytical isotopic analysis comes the need for well characterized reference materials designed to facilitate direct analyses of selective elements in geologic materials. Discussions will focus on USGS efforts to produce a synthetic basanite glass material (BPbISO-1G) spiked with NIST lead isotope standard SRM 981. Information will be presented on the procedure used to develop a special low lead concentration

blank glass, the dissolution of SRM 981, the spiking procedure used for the production of a 300 ppm (lead) glass material and the final USGS data compilation using LA-MC-ICP-MS and Thermal Ionization Mass Spectrometry (TIMS). Preliminary USGS LA-MC-ICP-MS analysis of the final 300 ppm lead glass demonstrates excellent agreement with the NIST SRM 981 certified values as seen in table 1.

Table 1. Comparison of lead isotopic composition in SRM 981 and BPbISO-1

Sample	²⁰⁸ Pb/ ²⁰⁴ Pb	±	²⁰⁷ Pb/ ²⁰⁴ Pb	±	²⁰⁶ Pb/ ²⁰⁴ Pb	±
NIST SRM 981 ¹	36.7219	0.0086	15.4916	0.0027	16.9374	0.0057
NIST SRM 981 ²	36.7219	0.0044	15.4963	0.0016	16.9405	0.0015
BPbISO-13	36.7201	0.0088 ^a	15.4950	0.0047 ^a	16.9446	0.0058 ^a

OP-32

Reference values following ISO guidelines for 20 most frequently requested rock reference materials

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The GeoReM database contains analytical data of most rock reference materials (RMs). There are also statistics about the most accessed RMs, such as BCR-2, BCR-1, BHVO-2, BIR-1, and JB-1. Although these samples are considered as being some of the most valuable RMs available, their reference values were not determined by metrological procedures. Exceptions, where a certification procedure was performed, are the slate OU-6 and the basalt BRP-1; however, these RMs do not belong to the top 20 most frequently requested rock RMs of GeoReM. We therefore established new reference values and their uncertainties at the 95 % confidence level for the 20 popular rock RMs following ISO guide 35 (2006) and the protocol of the IAG. In our study, we used all the analytical data from the GeoReM database published between 1995 and 2015. We are confident that we had access to a nearly complete data set for the last 20 years. The number of individual data for each rock RM varied between about 1000 (JA-1, JB-1) and 5000 - 6000 (BHVO-2, BIR-1, BCR-2). Partly more than 100 - 200 single analytical results (e.g., REE, Sr, Ba, Pb) were available for each RM. Reference values that are comparable to certified values in

a recertification programme were obtained by averaging the mean analytical results of the different laboratories. Some data were not used for these calculations, because they were inappropriately calibrated and/or have low precision and/or they did not fulfil the Horwitz requirement for outliers. Isotope dilution is considered to be a primary method having the highest metrological significance. Because of our use of literature values, where in some cases we are not able to judge the competence of the laboratory, we used at least 5 isotope dilution data from different laboratories to derive a reference value. In cases where less than 5 isotope dilution data exist, we averaged all data of techniques with a high level of confidence (e.g., ICP-MS, AAS, XRF). We report reference values, when they are derived from at least 7 laboratories and the number of methods is at least two. As an example, Table 1 shows the reference values for 4 USGS RMs. Whereas the concentrations of Ba, Sr, Nd and U are identical within 95 % confidence level for the pairs BCR-1 / BCR-2 and BHVO-1 / BHVO-2, respectively, they are significantly different for Pb and Mo, presumably because of sample contamination during preparation of the RMs.

Table 1: Reference values (µg/g) and uncertainties at 95 % confidence level

	BCR-1	BCR-2	BHVO-1	BHVO-2
Ba	683 ± 11	683 ± 5	134 ± 2	131 ± 1
Sr	335 ± 3	337 ± 6	399 ± 4	394 ± 2
Nd	28.7 ± 0.1	28.3 ± 0.3	24.8 ± 0.3	24.3 ± 0.2
Pb	13.4 ± 0.2	10.6 ± 0.2	2.13 ± 0.020	1.65 ± 0.04
Mo	1.52 ± 0.05	254 ± 6	1.05 ± 0.06	4.06 ± 0.17
U	1.68 ± 0.02	1.68 ± 0.02	0.418 ± 0.005	0.412 ± 0.025

OP-33

Optimization of rare earth analyses in geologic material using universal cell technology and ICP-MS

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The advantages of low detection limits and multi-element analyses make ICP-MS an indispensable tool for rare earth elements (REEs) analysis in soils, sands, clays, ashes, coals and other solid and liquid matrixes. However, low concentrations of REEs and complicated matrixes of coals and coal ashes can induce a significant amount of error in the analysis if the digestion of the sample is incomplete and detection modes are not optimized. In this study certified reference materials of coal, coal ash, and shale that were digested using a lithium metaborate fusion method and analyzed for REEs and other trace elements using ICP-MS with universal cell technology. ICP-MS methods tested for optimum REE recovery include standard operating mode as well as including kinetic energy discrimination (KED)

and dynamic reaction cell (DRC) modes. Each mode had advantages for certain rare earth elements indicating that using certain modes for specific REE may provide the most accurate method for analysis. The use of different modes for specific REEs is a relatively easy way to enhance the accuracy of REE measurements in coal and coal ash and may be a good technique for other complicated matrixes as well. The instrument used in this study is a Perkin Elmer Nexion 300D ICPMS. KED mode uses ultra-high purity helium while DRC applies ammonium and methane. For each complicated sample matrix, the exact conditions which optimize interference removal and maximize the signal for analytes of interest need to be experimentally determined.

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OP-34 Determination of organic-mineral composition of bazhenov formation rocks (West Siberia, Russia) by combination analytical technique

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The Bazhenov formation of the West-Siberian basin (Russia) is considered as the main source formation within the region. At the same time it is a major unconventional reservoir.

Promising challenge for oil companies is to optimize Bazhenov formation shale oil development, including the introduction of new methods of drilling and stimulation. Solving of these problems is impossible without the directory information on the composition of rocks and its change in the sequence. This work is devoted to developing an integrated method of studying the mineral component of the core samples. For clastic reservoirs determination of mineral composition is performed using X-ray methods, while in the Bazhenov formation rocks their direct application is difficult. Primarily because of a great amount of organic material which has an undefined composition and an amorphous form. Secondly, the rocks may contain opal, which is undetectable by XRD. The third problem is to determine the types of clay minerals: hydromica and mixed-layer minerals [1].

The technique of organic-mineral composition determination of the rocks containing X-ray amorphous minerals and kerogen has been developed. At the first stage samples are studied by XRF analysis.

Then mineral with crystal lattice composition was determined using XRD. The most important information is the calcite-dolomite ratio due to isomorphic substitution of calcium and magnesium in these minerals.

The composition of clay minerals was determined by SEM with a special attachment for X-ray microanalysis.

To determine the amount of kerogen pyrolysis of

samples by the method of Rock-Eval was conducted [2, 3].

On the next stage kerogen was recovered from core examples and analyzed by ICP-SM to determine its composition.

Based on the measured data the composition of the rocks obtained by XRF was converted to calculate the amount of the following components:

- calcite and dolomite
- kerogen
- clay minerals and mixed-hydromica.

The remaining element amounts were used to calculate siliceous minerals, pyrite and albite. Thus, a combination technique that includes XRD, XRF, Rock Eval pyrolysis, SEM and ICP-SM was determined in this work. It allows evaluating the content of all minerals and amorphous components. This techniques allowed to determine that the main rock-forming components of Bazhenov formation are siliceous (60-90%), clay (<25-30%, average 10%), and carbonate minerals - calcite, dolomite, siderite (in some interlayers they can reach 95%), and organic matter (<30%, on average 5-15%).

After setting up the interpretation of log data information on the material composition of the rocks would allow to solve a wide range of problems in development of bazhenov formation shale deposits.

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POSTER SESSION

P-01

Integration of Electrical Resistivity Tomography and GPR for Sinkholes Detection in Al-Rufa'a Area

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Natural voids and cavities in subsurface karstic limestone cause environmental and engineering problems for urban extension. In the present study, 2D-electrical resistivity tomography integrated with ground penetrating radar (GPR) methods is used for detecting and delineating the possible karstic features in Al-Rufa'a area. This area is located to the southeast of Riyadh City and is considered a part of the Rufa'a Graben and its skirting Jibal Jubayl escarpment. This area suffers from karstic features, such as sinkholes, solution cavities and voids.

2-D electrical resistivity and GPR data sets have been acquired along six profiles in a new urban extension

site. Dipole-dipole electrode array using 5 m electrode spacing and 400 MHz antenna was used during the resistivity survey and GPR imaging, respectively. The results showed soil-fill and air-fill cavities that extend vertically and/or laterally at shallow depths in the studied area. These cavity features are distinguishable by being a relatively very high resistivity zone in case of air-filled cavities and turned into a conductive one with low resistivities in some places where the cavities are filled with soil. This suggests that the detected karstic features could strongly affect the planned surface and subsurface infrastructures in this new urban expansion site.

P-02**Neutron activation analysis of urban soils from Mongolia**

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Environmental science is the multidisciplinary field that integrates range of disciplines to study of the environment and emerging problems within it. An applied nuclear physics method, i.e., Instrumental Neutron Activation Analysis (INAA), for an example, was used in this survey to investigate distributions of heavy metal and some toxic elements in Ulaanbaatar soils. Total of 41 soil elements were analyzed for their distribution in rural soils by INAA using epithermal neutrons at the IBR-2 reactor, Frank Laboratory of Neutron Physics, JINR. The obtained results were

compared to abundance of species in the earth upper crust and data for Mongolian urban soils, considered as pristine area.

The objective of this study was to determine the concentrations of a wide range of elements including heavy metals and trace elements at the selected sites with the possible sources of the pollutants, and to compare with the elemental distributions in the earth upper crust and Mongolian rural soils.

P-03**The reconstruction of paleo-environment Albo-Aptian sediments of the massive El Hmaima North Tébessa**

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The research work will be continue for a correlation between the Albo-Aptian across North Africa to focused on sedimentological, tectonic and paleontological study of Albo-Aptian formations massive El Hmaima-North of Algeria.

A systematic study was then initiated consisting of the sampling in a washing furniture samples of some Albian levels, and a careful sorting of microfossils and

minerals under the lens of binocular microscope. Hard samples Aptian were processed by making a thin section to help determine as precisely as possible the characteristics of the levels studied. The material used is existing in geology lab. Tébessa University, Algeria. The massive El Hmaima North Tébessa was located on the territory of the municipality of Boulhef Dyr, Daira of Morsott.

P-04**Impact of Heavy Metals Pollution on Continental Water Resources: a Case Study in El-Minia Province, north Upper Egypt****ESAM ISMAIL¹, RAFAT ZAKI, WAGIH MOHAMED, ALI KAMEL**¹Geology Department, Faculty of Science, Minia University, El-Minia (Egypt)

Hydrogeochemical survey and cluster analysis have been conducted on surface water and groundwater from El Minia Province, north Upper Egypt to study the possible impact of heavy metals pollution on drinking water and its effects on human health. Concentration of heavy metals (e.g., As, Co, Hg, Ni, Se, Cd and Cr) in surface water and groundwater samples is most significantly affected by leachate of many pollutants. On the other hand, the Fe, Cu, Mn, Pb, Zn and B that derived from anthropogenic influences (in El Moheet drain and its branches),

where its septic tanks are affected by the factories, agricultural activities and urban at Abo-Qarqas, El Minia and Maghagha areas as well as natural processes (such as changes in precipitation inputs, erosion, weathering of Pliocene and Eocene rocks).

Microbiological parameters and microscopic investigations are revealed that some localities are common by micro-organisms, which are unsuitable for drinking waters.

P-05**Elemental analysis in archaeometric study of pottery of Yaz II culture from northern part of Serakhs oasis, south of Turkmenistan****LUIZA KĘPA¹, MARCIN WAGNER², BARBARA WAGNER¹, MAGDALENA GÓRSKA³**¹Biological and Chemical Research Centre, University of Warsaw (Poland)²Institute of Archaeology, University of Warsaw (Poland)³Faculty of Chemistry, University of Warsaw (Poland)

Elemental composition of ceramic materials from archaeological sites, located in northern part of Serakhs oasis in Turkmenistan, was investigated in detail. The aim of this research was to compare pottery sherds from five sites (Ara depe, Atsyz depe 2, 3, and 5 and Oyukly depe). Four of them are smaller satellite sites located around the biggest Oyukly depe, which was an administrative center of Serakhs oasis at the beginning of 1st millennium BC. During two surveys (2008-2009) and excavated season in 2012 at Oyukly depe many of pottery sherds typical for Yaz II culture were found. Results of archaeometric analysis of mentioned pottery will be compared with ceramic finds from Topaz Gala depe, where remains of Zoroastrian fire temples were excavated, dated to the same period.

Inhomogeneous chemical and structural composition of ceramics create difficulties for analytical studies although a lot of important information for the history of its creation is hidden there. Dissolving of samples would have caused the loss of important information about spatial distribution of minerals/elements in the sample, as well as might have resulted in the loss of information about trace elements, which can have key role in determining the provenance of the sample.

Therefore, during the study of historical ceramics from Turkmenistan portable X-ray fluorescence (pXRF, Tracer III-SD, Bruker) was used to evaluate the bulk elemental composition before Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) detailed measurements. LA-ICP-MS is a method with low detection limits and ability to obtain information about isotopic/elemental distribution over samples' surface of solids.

Bulk analysis by means of XRF allowed to compare the main elemental composition for the objects taking into account Al, Si, P, S, K, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Zr detected in ceramic materials. More detailed study involving spatial distribution of the selected elements was carried out by means of LA-ICP-MS (CETAC LSX-213 coupled to NexION 300D, Perkin Elmer) and monitoring of transient signals for: ⁷Li, ²³Na, ²⁶Mg, ²⁷Al, ²⁹Si, ³¹P, ³²S, ³⁵Cl, ³⁹K, ⁴²Ca, ⁴⁵Sc, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶¹Ni, ⁶³Cu, ⁶⁶Zn, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹⁵Mo, ¹²⁰Sn, ¹²¹Sb, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶¹Dy, ¹⁷⁹Hf, ²⁰⁸Pb, ²⁰⁹Bi, ²³²Th, ²³⁸U. NIST 610 was the external standard while SRM 679 (brick clay) was used to control the quality of the final quantitative results. Both the precision and accuracy were satisfactory.

Recognition of two variable groups of objects was proposed on the basis of the obtained quantitative elemental results supported by mapping of the elemental distribution over the investigated artefacts. The chemical analysis supported the archaeological knowledge about the use of homogeneous ceramic with few exceptions, which were identified in this research.

Acknowledgements

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P-06

Characteristics of marine Co-rich ferromanganese crusts of the South Atlantic through the distribution of the rare earth elements

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The study of rare earth elements became important from the mineralogical and economic aspect, from 1839 when there was the first studies of its most important features as economic sources: minerals bastnasite, monazite, loparite, and lateritic clays. The main phases of Co-rich crusts are Fe-bearing vernadite and Fe oxo-hydroxides. Thick crusts may contain carbonate-fluorapatite (CFA) as well as low amounts of quartz and feldspar.

There are earth elements are incorporated into applications such as superconductors, miniaturized magnets, catalysts used in refining various products, components for hybrid cars and in cathode ray tubes for televisions and computers.

The uses mentioned above and the growing demand for rare earth elements for this type of applications, the Rio Grande Seamount, South Atlantic, arises an great strategic political and economic and is located outside the 200 nautical miles off the Brazilian exclusive economic zone (an International areas). One of the possible sources of rare earth elements are cobalt-rich seamount ferromanganese crusts in Rio Grande Seamount.

Determination of rare earth elements and Y by ICP-MS analysis will be presented and evaluated in this work with support of petrographic lamination (and reflected polarized light), Scanning Electron Microprobe (SEM), X-ray Diffraction (XRD) and X-ray

Fluorescence (XRF). Typical patterns of rare earth elements in crusts and polymetallic nodules of marine environment are classified on: Mn hydrothermal deposits, Fe-Mn crusts hydrogenetic, Fe-Mn diagenetic Nodule, Fe-Mn crust phosphate and Fe-Mn Nodule hydrogenetic, in accordance with the positive and negative anomalies of Ce and Y.

The formation of crusts is usually ascribed to the oxidative scavenging of Ce and its preferential removal from seawater by hydrous Fe-Mn oxides. The close association of Ce and Fe corroborates the role of hydrous Fe oxides as an oxidative scavenger from seawater. In recently published work has suggested that the rare earth elements present in environments containing crusts and polymetallic nodules are formed during the process of chemical precipitation of oxides and hydroxides of Fe and Mn, with Ce positive anomaly.

In this study the rare earth elements and Y were normalized relative to PAAS method (Australian Post Archean shale) and can be noticed that most presented as a result of the predominance of positive anomalies in Ce and Y.

Behavior that characterizes the polymetallic crusts formed in this region would be hydrogenetic. And compared to other international marine environments (as compared to the Eastern Pacific, South China Sea, Pacific NE) the mean values are satisfactory.

P-07

Characterization of volcanic ashes from ~4200 BP Cerro Blanco eruption-Central Andes using LA-HR-ICP-MS and EPMA

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Following the results obtained of geochemical studies of volcanic ashes from Cerro Blanco Volcanic Complex (CBVC) in the Central Andes of NW Argentina we can delimitate and isolate a major eruption in the CBVC. We estimate that this eruption spreading ~110 km² ashes over 400.000 km²- long thought to have. This fact confirms that this eruption may be the biggest during the past five millennia in the Central Volcanic Zone of the Andes, and possibly one of the largest Holocene eruptions in the world (Fernandez-Turiel *et al.* 2013).

One of the main problems that we have studying volcanic ashes is that its grain size of the particles is lower than 2 mm and the bulk analysis can hide the actual signature of the original magmatic material and the other is the similar features of these deposits on the outcrops. Bulk analyses reflect the mixture of geochemical signature from the original material (volcanic glass) and fragments of the local host rock. The identification of ash particles from a determined eruption may be solved applying techniques of microanalysis to several single volcanic particles. Electron microprobe analysis (EPMA) provides excellent results for analysis of major elements, but the detection limits are not suitable for the determination of many trace elements. The sampling of particles by laser ablation (LA) and subsequent analysis by ICP-MS (LA-ICP-MS) is a method of great potential for the analysis of trace elements on volcanic glass fragments.

We have analysed the volcanic ash particles (volcanic glass) from more than 100 sites using a NewWave Research UP 193 excimer laser ablation system coupled

to an Element XR HR-ICP-MS (Thermo Scientific). The isotopes analysed by LA-HR-ICP-MS were ⁷Li, ⁹Be, ¹¹B, ²³Na, ²⁴Mg, ²⁷Al, ²⁹Si, ³¹P, ³²S, ³⁵Cl, ³⁹K, ⁴³Ca, ⁴⁵Sc, ⁴⁹Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷⁴Ge, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ⁹⁸Mo, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶²Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷⁴Yb, ¹⁷⁵Lu, ¹⁷⁶Hf, ¹⁸¹Ta, ¹⁸²W, ²⁰⁸Pb, ²³²Th, ²³⁸U.

The EPMA analyses were carried out using a Cameca SX-50 electron microprobe and the oxides analysed were Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, Cr₂O₃, MnO, Fe₂O₃, NiO, ZnO, BaO. The best strategy is to use the major elements by EPMA (more accurate for major elements due to better availability of reference materials for EPMA) and the trace elements obtained by laser ablation (²⁹Si as internal standard, and, NIST 612, glass DVA-1G and 2402 obsidian rock as RM).

All the studied volcanic ashes have a rhyolitic composition, but the analysis of A/CNK ratio [(Al₂O₃/CaO+Na₂O+K₂O) mol %], and the analysis of REE (rare earth elements) confirms the existence of two different eruptions (one ~ 4200 BP and other more ancient). Ratios between Eu/Eu* (Eu-anomaly), Sm/Yb, and Sr/Rb of isolated volcanic glass particles contributed to characterize each eruption and determine the area affected by the ~4200 BP Cerro Blanco eruption.

Financial support was provided by the QUECA Project (MINECO, CGL2011-23307). Analyses were carried out in the Geochemistry Facility of labGEOTOP in the ICTJA-CSIC, infrastructure co-funded by ERDF-EU (Ref. CSIC08-4E-001). We acknowledge to X. Llobet the assistance in the EMPA analysis at the CCIT-UB facilities.

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P-08

Cloud point extraction for the determination of platinum group elements in moss samples by ICP-MS

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The use of palladium, platinum and rhodium in catalytic converters of automobiles has led to emissions of these metals to the environment. Monitoring of these traffic-related emissions has been conducted for example from road dust, soil and plant samples (e.g., Fritsche and Meisel 2004, Pan *et al.* 2009, Whiteley and Murray 2003). Among plants, mosses can be used for active monitoring of these emissions, because they obtain most of their nutrients directly from rainwater and dry deposition (Niemelä *et al.* 2007). However, the concentrations to be determined are low. Additionally, the determinations of Pd, Pt and Rh using quadrupole ICP-MS (Q-ICP-MS) may be interfered by the matrix elements of the samples. For example, the formation of molecular ions, such as ⁸⁹Y¹⁶O⁺ and ⁸⁸Sr¹⁶O¹H⁺, may cause spectral interferences in the determination of ¹⁰⁵Pd (Djingova *et al.* 2003).

Usually, mathematical correction or separation methods are needed when platinum group elements (PGEs) are determined in environmental samples by Q-ICP-MS. Cloud point extraction (CPE) with suitably selected conditions (e.g., surfactant, complexing agent, temperature, extraction time, etc.) can be used

in separation of metals (e.g., PGEs) from interfering matrix elements. Generally speaking, in CPE, neutral metal complexes are extracted from acidic aqueous sample solutions (e.g. microwave digested samples) to small volume surfactant-rich phases obtained by heating (Bezerra *et al.* 2005).

The aim of this study was to develop an interference-free method for the determination of Pd, Pt and Rh in moss samples. Thus, microwave-assisted digestion was combined with a CPE method. To evaluate the suitability of microwave-assisted *aqua regia* digestion/leaching, two certified reference materials, SRM-2557 (used auto catalyst) and BCR-723 (road dust), were added to moss samples prior to the digestion. The samples were analyzed both after the microwave digestion and after the samples had been treated with CPE. The CPE method appeared to be effective in interference elimination. The results obtained for the spiked moss samples after *aqua regia* digestion and CPE were in agreement with the expected values for Pd, Pt and Rh (Table 1). The results indicate that this approach can be used in the analyses of moss samples with traffic-related emissions of Pd, Pt and Rh.

Table 1. Expected and determined ($n = 3$) concentrations for Pd, Pt and Rh in moss samples spiked with reference materials.

Material	Element	Unit	Expected	Determined
BCR-723	Pd	µg/kg	6.0 ± 1.8	6.3 ± 0.9
	Pt	µg/kg	81.3 ± 3.3	76 ± 10
	Rh	µg/kg	12.8 ± 1.2	13.7 ± 1.9
SRM 2557	Pd	mg/kg	233.2 ± 1.9	209 ± 6
	Pt	mg/kg	1131 ± 11	1035 ± 43
	Rh	mg/kg	135.1 ± 1.9	93 ± 16

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P-09

LA-SF-ICP-MS U-Pb zircon dating at University of Campinas, Brazil

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Recently, the Isotopic Geology Laboratory at Campinas State University has incorporated an Excite.193 (Photon Machines) laser ablation system, equipped with a two-volume HelEx ablation cell, coupled with an ICP-MS Element XR (Thermo Scientific). This work describes the analytical configuration for U-Pb zircon dating routine.

Zircon grains were mounted in 1 inch round epoxy mounts resin, polished using diamond paste and cleaned using 10% v/v HNO₃ followed by de-ionized water.

The acquisition protocol adopted was: 30 s of gas blank acquisition followed by the ablation of the sample for 60 s in ultrapure He (laser frequency at 10 Hz, spot size of 40 μm and laser fluence of 4.74 J cm⁻²). Data were collected for masses 202, 204, 206, 207, 208, 232, 235 and 238 using the ion counting modes of the SEM detector, except for masses 232 and 238, which were analyzed in combined ion counting and analogue mode. Four points were measured per mass peak, and the respective dwell times per mass were 4, 8, 4, 16,

4, 4, 4 e 4 ms. Data were reduced off-line using Iolite software (version 2.5) following the method described by Paton *et al.* 2010, which involves subtraction of gas blank followed by downhole fractionation correction comparing with the behavior of the 91500 reference zircon (Wiedenbeck *et al.* 1995). Common Pb correction was accomplished using VizualAge version 2014.10 (Petrus and Kamber 2012) when necessary.

Zircon reference samples Plešovice, Peixe, Temora and SriLanka, analyzed as unknown samples during this study, yielded concordia ages of 346 ± 1, 562 ± 2, 418 ± 2 and 567 ± 2 Ma respectively, which agree with the published values. An in house zircon sample submitted to the same procedure yielded a concordia age of 3314 ± 3 Ma, in agreement with previously age determined by SHRIMP (3310 ± 7 Ma).

In addition to dating, Iolite allowed to determine the total approximated concentrations of U, Th, Pb in the same spot. The results here observed are also in agreement with those reported in the literature.

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P-10

Carbon and oxygen isotopic geochemistry of paleoproterozoic carbonates from Fecho do Funil Formation – Iron quadrangle - Brazil

LEONARDO NOGUEIRA¹, HERMÍNIO NALINI JR¹, NEIL BANERJEE², MARIANGELA LEITE¹¹Federal University of Ouro Preto (Brazil)²University of Western Ontario (Canada)

Carbon and oxygen isotope studies of carbonate rocks have provided knowledge into Precambrian seawater chemistry (Perry and Tan 1972, Veizer *et al.* 1992a). Much of the recent work has determined δ¹³C and δ¹⁸O values of Precambrian carbonate sequences to understand the depositional processes, the evolution of the ocean-atmospheric system, and the interactions of biotic and abiotic processes during the Earth's history (Burdett *et al.* 1990, Veizer *et al.* 1992a,b, Knoll *et al.* 1995). Carbonate sediments deposited between 2.4 and 2.0 Ga are particularly important because they record an unprecedented positive δ¹³C excursion originally reported by Schidlowski *et al.* 1976 from carbonates of the Lomagundi Group, Zimbabwe. Carbon and oxygen isotope fluctuations in Precambrian sedimentary carbonates from Fecho do Funil Formation – Iron quadrangle - Brazil are examined in this study. With the purpose of obtaining the carbon and oxygen isotopic data, a 40 meters thick carbonate section of carbonates rocks (Fecho do Funil Formation) were sampled in the Cumbi Quarry about 11 kilometers south of the town of Cachoeira do Campo in the north-central part of the Dom Bosco Quadrangle, center-south region of the Quadrilátero Ferrífero. Thirteen carbonates samples were collected for whole rock analyses. The samples were prepared and isotope analyses were carried out at the Laboratory Stable Isotope Science (LSIS) of the University of Western Ontario, Canada.

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Carbon and Oxygen isotope composition from whole carbonates rocks were obtained by close tube reaction with orthophosphoric acid (100%) at 90° C using a Micromass Multiprep device coupled to an Optima Dual Inlet, triple collecting Isotope ratio Mass Spectrometer. The external precision was based on multiple standard measurements of NBS-19, NBS-18 and LSVEC. The results are expressed in the δ notation in parts per thousand (‰) in relation to the international V-PDB scale. The Paleoproterozoic Fecho do Funil Formation, displays a narrow δ¹³C_{VPDB} (+6.02 to +7.23 ‰) and δ¹⁸O_{VPDB} (-11.22 to -10.42 ‰) compatible with carbon and oxygen isotope signatures of sedimentary carbonates deposited around 2.1 Ga, similar to other successions deposited during the Lomagundi event. The values found in this work for δ¹³C_{VPDB} probably reflect seawater composition during the Lomagundi Event. Normally, carbon isotope composition do not change significantly during diagenesis. This is because carbon content in carbonate rock is vastly greater than that in porewater reservoir and because the fractionation between calcium carbonate and water is relatively small at near-surface temperatures. We infer that the elevated carbon isotope values of the Fecho do Funil carbonates likely reflect primary carbon isotope composition. The chemostratigraphic data allowed correlate this succession with others successions with equivalent age around the world.

P-11

High precision in-situ Pb isotope analyses by LA-MC-ICP-MS using a USGS synthetic basalt glass (BPbISO-1) spiked with NIST SRM 981

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The accuracy and precision for laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) determinations of Pb isotope ratios is limited due to the lack of solid in-situ isotopic reference materials. Numerous mass bias correction methods are used for Pb isotope analyses by LA-MC-ICP-MS including: 1) simultaneous aspiration of NIST SRM 981Ti solution via a desolvating nebulizer system; 2) standard-sample bracketing (SSB) with NIST SRM 610, 612 or an in-house Pb isotope reference material; 3) SSB with SRM 610 or 612 and externally reporting the differences to NIST SRM 981 solution results as deviation from SRM 981 in per mil notation. For TI mass bias correction the measured fractionation factor (f) for TI is then applied to Pb. However, previous studies for solution MC-ICP-MS have suggested that f for TI and Pb are not equal over the range of Pb isotope pairs, and the use of a TI correction requires additional external normalization to incorporate variations in f , as well as behavioral differences during vaporization,

atomization, and ionization. Additionally, simultaneous aspiration of SRM 997 TI during laser ablation analyses possibly introduces differences in mass bias between the two systems. The use of SRM 610 or 612, although thoroughly evaluated, has resulted in a range of isotopic composition without a consensus value. The use of BPbISO-1 also eliminates the need for TI addition and provides for the direct isotope pair mass bias correction using the well-established Pb isotope reference material, SRM 981. Our study reports on the new Pb isotope reference material developed at the USGS (BPbISO-1) made by spiking a synthetic basalt glass with SRM 981 Pb and using it to correct Pb isotope pair (e.g. $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$) mass bias during in-situ Pb isotope ratio measurements (Table 1; preliminary results for SRM 610). The use of BPbISO-1G for the isotopic analyses of Pb in additional USGS and other international reference materials will also be presented.

Table 1: Comparison of preliminary NIST SRM 610 Pb isotope ratio results using BPbISO-1 to previously published values.

	SRM 610 $^{208}\text{Pb}/^{204}\text{Pb}$	SRM 610 $^{207}\text{Pb}/^{204}\text{Pb}$	SRM 610 $^{206}\text{Pb}/^{204}\text{Pb}$
BPbISO-1 method	36.967 ± 5	15.507 ± 3	17.040 ± 2
Preferred values ¹	36.964 ± 22	15.504 ± 9	17.045 ± 8

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P-12

Martin Vaz Island Ar-Ar dating, South Atlantic, Brazil

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Martin Vaz Island is one of the oceanic islands related to the Vitória-Trindade Ridge, an important South Atlantic physiographic feature. Located at the latitude 20°28'28"S and longitude 28°51'05"W, about 1200 km from the Brazilian coast. Its geology is an important preserved record of a Pleistocene alkaline volcanic activity. It stands out geological features associated with volcanic relief such as phonolitic necks and dikes and sub-horizontal layers formed by pyroclastic rocks and lava flows (basanites) (A.C. Santos *et al.*, 2015).

Few geological studies were performed in Martin Vaz, mainly by its access difficulty. It stands out from Cordani (1970) with the first geochronological dating. Further works as Hansen *et al.* (1998) and Siebel *et al.* (2000) presented the plume evidences from chemical, petrological and geochronological analyses. Both mention the presence of lava flows, dikes, phonolitic necks, pyroclastic rocks and ultrabasic. Hansen *et al.*, (1998) have a Martin Vaz K-Ar age of 1.1 ± 0.5 Ma.

Samples were dated at Curtin University, Perth, Australia, using the Argus Mass Spectrometer by step-heating. It was analyzed 06 samples for Martin Vaz.

The samples MVA-07, MVA-10 and MVA-14 are representative of the basanite flow that covers the top

of the island. They present plateau ages ranging from 320 ± 366 Ka to 721 ± 322 Ka. The samples MVA-10 and MVA-14 have different ⁴⁰Ar-³⁹Ar age spectra.

It is noteworthy that the MVA-07 sample shows the spectrum of ⁴⁰Ar-³⁹Ar ages more homogeneous being calculated one plateau age of 492 ± 87 ka (MSWD = 1.4 and probability = 0.21). Also the respective sample was the only one from the basanite flow in which it was possible to establish an inverse isochron obtaining a similar age of 451 ± 121 ka.

The MVA-05 and MVA-05B samples are phonolites dikes. They present plateau ages respectively 440 ± 126 Ka and 649 ± 84 Ka and inverse isochron of 316 ± 149 Ka and 609 ± 128 Ka.

The MVA-04 sample is representative of the Martin Vaz Island central volcanic neck. It displays Ar-Ar age plateau of 623 ± 127 ka and 594 ± 132 Ka reverse isochron.

These ages show the youngest Brazilian rock during Pleistocene volcanism in the South Atlantic Ocean and even not clear the correlation ages between the basanites and the phonolites, field evidences show the last ones cross cutting the first ones.

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P-13**Detection of metals and rare earth elements in deep eutectic solvents and ionic liquids using ICP-MS****TRACY BANK¹, ELLIOT ROTH, MEGAN MACALA, EVAN GRANITE**¹AECOM, Pittsburgh (USA)

Ionic liquids and deep eutectic solvents (DESs) are ionic solvents that have interesting solvent properties for metals and metal oxides. One of the first deep eutectic solvents studied was a 2:1 mixture of urea and choline chloride which was shown to be able to dissolve metal oxides. This ability makes ionic liquids an interesting medium for metal extraction from complicated solid matrices. The ability to accurately measure trace concentrations of base metals and rare earth elements in ionic liquids is important to the study of rare earth element extraction processes.

In this study, a common ionic liquid (emim Tf2N) was spiked with low and varying concentrations of metals and rare earth elements (from 1 ppt to 10 ppb) and the concentrations of the elements were measured using ICP-MS with universal cell technology. Different digestion techniques with various acid concentrations

were studied and the recoveries of elements using different ICPMS modes were determined. Preliminary results indicate that digestion is best accomplished with weak nitric acid and 90-100% recovery of spiked concentrations is typical.

The results of metal extraction using the same ionic liquid (emim Tf2N) with fine ash, coarse ash, and lignite coal mixed together for 3 hours at room temperature showed promising results. In fact this non-optimized ionic liquid with a short contact time, low concentration of ionic liquid, and at room temperature showed up to 10% extraction of some of the rare earth elements. Additionally, it appeared to selectively extract the more important heavy rare earth elements compared to the light rare earth elements.

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P-14**Mineralogical and chemical analysis of secondary raw materials - challenges and pitfalls****SANDRA DRESSLER¹, KAI BACHMANN¹, AXEL D. RENNO¹, OLIVER SCHARF², JULIANE SCHAEFER**¹Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Freiberg (Germany)²IFG Institute for Scientific Instruments GmbH, Berlin (Germany)³UVR-FIA GmbH, Freiberg (Germany)

Secondary raw materials (SRM) are becoming increasingly more important in ensuring the stability of critical metal supply. Like for natural raw materials, processing and metallurgical treatment demands a detailed and meticulous geometallurgical characterisation. Unlike municipal solid waste and Waste Electrical and Electronic Equipment (WEEE), ashes, slags, dusts and other industrial residues are "produced" centrally in large quantities. In light of these circumstances, the logistics of supply is simpler. This makes these types of SRM ideal candidates for the extraction of critical metals.

Precise and accurate chemical and mineralogical data, knowledge of distribution of valuable and deleterious elements in the single phases as well as information about homogeneity and grain size distribution of

the minerals are crucial for the development of new extraction technologies. Gaining these essential information can be achieved by using SEM-based automated mineralogical analysis. However, the large particle size range, the dominance of very small grain sizes (< 5 µm) and the diversity of phases are challenging for the analysis. Furthermore, in contrast to natural materials the analysis of secondary materials faces the challenge of developing new methods for non-natural extreme combinations of elements and phases. To overcome these challenges we used complementary analytical methods, like XRD and optical microscopy. Two of them, High-Speed PIXE and the "MEGA" instrument are still in the stage of development. Both instruments deliver additional information about trace element distribution.

P-15

SelfSeal sample chamber: automation for industrial bulk analysisKATHERINE MCLACHLIN², SHANE HILLIARD, CIARAN O'CONNOR, ROB HUTCHINSON¹, JAY WILKINS¹ Electro Scientific Industries, Europe Ltd., Huntington, (UK)² Bozeman (USA)

Elemental analysis to support mineral exploration requires accurate, precise and low detection limits, with an ability to meet high sample throughput demands. With respect to analytical figures of merit, LA-ICP-MS is an excellent fit. However, the current level of human intervention limits its ability to meet throughput requirements and thus the technique has not been widely adopted in the industry.

The most common approach for improving LA-ICP-MS throughput is to utilize large sample chambers that are capable of holding a large number of samples at a time. This approach is non-ideal, however, as simply utilizing a large sample chamber fails to address the time and human involvement of placement of samples, purging, and focusing scans. Depending on the samples, this can take nearly as long as the analysis itself.

Additionally, recent studies have demonstrated that increasing the sample chamber dimensions without accounting for gas flow dynamics can

either dramatically increase the purge time (actually decreasing throughput) or decreasing positional reproducibility (increasing error). Even large sample chambers that are capable of rapid, efficient purges, such as the TwoVol2, require manual placement of samples and focus adjustments. Samples may also be cut, to increase the volume per batch, but this adds sample prep time and makes traceability more complex.

To reduce the time and human involvement between analyses, ESI has developed the SelfSeal sample chamber, specifically for true high throughput sampling of industrial materials. The SelfSeal chamber requires no focusing time, no pattern adjustment, has a purge time of under 7 seconds, and maintains the positional stability and sensitivity expected of LA-ICP-MS. Here we demonstrate calibration curves on real XRF standards and repeatability figures on NIST glass, as well as providing a full analysis time from sample introduction to sample removal and realistic estimates of maximum samples per day.

References:

ESI Technical Note: NWR025 Comparison of Laser Ablation Cell Purging Techniques

P-16

Raman investigation of human dental hard tissues affected with dental diseases of different etiologyDARIA KISELEVA¹, SVETLANA LEBEDEV², JULIA MANDRA³, NATALIA OZHGIHINA³¹Institute of Geology and Geochemistry UB RAS, Ekaterinburg (Russia)²Institute of Mineralogy UB RAS, Ilmenny state reserve, Miass (Russia)³Ural State Medical University, Ekaterinburg, (Russia)

Spectroscopic techniques (in particular, Raman spectroscopy) are widely used to study the local molecular structure and its defects in organic-mineral aggregates of human bone and tooth tissues (Tarnowski *et al.* 2002, Ager *et al.* 2006).

Raman spectroscopy is a nondestructive vibrational spectroscopic technique that permits the study of organic and mineral species at micron resolution, offers the ability to work with hydrated and dehydrated specimens, and requires minimal specimen preparation (Tarnowski *et al.* 2002).

The aim of our study was to investigate human dental hard tissues by means of Raman spectroscopy concerning the differences between intact (sound) teeth and teeth affected with dental diseases of different etiology.

Samples. Extracted permanent and deciduous (molars and premolars) teeth were obtained from the dental clinic of Ural State Medical University, Ekaterinburg. The samples were categorized into groups according to dental diseases of different etiology: teeth with caries lesions, teeth with increased abrasion, teeth with hypoplasia lesions of different severity (white spots and yellow or brown teeth), and intact (sound).

Raman spectroscopy. Raman spectra were collected using LabRam HR Evolution (Horiba, Institute of Geology and Geochemistry UB RAS, Ekaterinburg)

and iHR 320 (Horiba, Institute of Mineralogy UB RAS, Miass) with excitation lasers of 633 nm in the range of 200-3500 cm⁻¹. Digital spectra were processed with PeakFit V.4.11, smoothed, background corrected, and summary peaks were deconvoluted into elementary components.

The Raman spectra of enamel and dentin are dominated by spectral contributions of the mineral matrix. Bands at 431, 591, 608, 960, 1044 and 1071 cm⁻¹ are assigned to phosphate vibrations of hydroxyapatite. The most intense band at 960 cm⁻¹ is the symmetric stretch vibration of PO₄³⁻.

Integral ratios of major component bands (hydroxyapatite, amide I and B-type carbonate) were used for evaluation of mineralization degree, degree of crystallinity, relative fractions of B-type carbonate, disordered and highly crystalline non-substituted phosphate.

According to obtained data, all investigated samples consisted predominantly of B-type carbonated hydroxyapatite with its highest content in intact teeth, and lowest in carious. Carious dental tissues were found to contain the biggest amount of disordered phosphate (A-type or amorphous calcium phosphate).

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P-17

Advantages and disadvantages of femtosecond 200 nm laser ablation-ICP-mass spectrometry for trace element analysis

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Kupferschiefer, i.e. very fine-grained and disseminated polymetallic Cu-Ag ores of the extensive stratabound deposits of the Central European Copperbelt is well known for its mineralogical complexity and the challenges surrounding its characterization. It is marked by a combination of high metal sulfide contents (up to 25 wt%) and organic matter (up to 30 wt%) within a matrix predominantly composed of fine-grained clay and carbonate minerals. Conventional analytical procedures often yield unreliable results of this very complex raw material. Regardless, recent research into the hydrometallurgical and microbiological beneficiation of Kupferschiefer has raised the demand for supplying reliable quantitative data of the mineralogy and the geochemistry for both the raw material and process samples. A research project was thus initiated to establish a robust analytical procedure to quantify both mineralogical as well as geochemical attributes of Kupferschiefer-type ores. A combination of analytical techniques is employed for this purpose, including quantitative X-ray diffraction (QXRD), image analysis based on scanning electron microscopy/mineral liberation analysis (MLA), XRF, ICP-AES, and INAA. Method development was based on selected Kupferschiefer samples obtained from Sangerhausen (Germany) and Polkowice-Sieroszowice (Poland) deposits. QXRD by Rietveld refinement is particularly well-suited to determine the modal mineralogy of fine-grained samples. Five types of layer silicates were identified in Kupferschiefer samples. These are being characterized in detail in order to build crystal structure files needed to enable a full quantification of the minerals present. The necessary characterization

of this set of layer silicates has been inhibited by the presence of organic matter, requiring chemical pre-treatment of the raw material that is specifically developed for this purpose. SEM-based mineral liberation analysis (MLA) on grain mounts of crushed aliquots of the powder samples used for QXRD is used to verify mineral identification and to determine the amounts, liberation, and types of sulphide minerals contained in the samples. This technique is not suited to determine the abundance of the silicate minerals due to their fine-grained and intimately intergrown texture. Further obstacles, such as misidentification of disordered carbonate minerals by XRD or copper sulfides by MLA, are encountered often and can only be recognized and minimized by verifying results using multiple analytical methods. Independent observations from microscopy or bulk geochemistry by fusion XRF are useful in ensuring a high data quality and to test for consistency. Whole rock trace element data are acquired using INAA, XRF, and ICP-OES. While INAA can guarantee a full analysis without requiring a problematic digestion treatment, the procedure itself is not available for routine measurements. XRF analysis of pressed pellets has been inhibited by the variable content of organic material and matrix effects caused by high sulfide concentrations. ICP-AES/MS analysis is considered to be the most appropriate technique in this case. Different combinations of hydrogen peroxide, nitric acid, and perchloric acid digestion techniques are tested to identify an optimal procedure for the acid digestion of the diverse sulfide compounds as well as the organic matter contained in Kupferschiefer.

P-18

Using portable X-Ray fluorescence to identify the K-Pg boundary in terrestrial records

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The K-Pg boundary (KPgB) has been identified in a large number of marine sections all over the world. For this purpose, numerous works report micropaleontology (mass-extinction) data, geochemical analyses (stable isotopes and trace elements such as iridium) and observations of microkrystites (spherules). In terrestrial sections, however, the KPgB has only been identified in locations relatively close to the impact area (like the USA and Canada) and in a lacustrine setting in New Zealand. The unambiguous identification of the KPgB in distal terrestrial sections remains very challenging.

In the present work we explore the usefulness of portable X-ray fluorescence (pXRF) spectrometers to delimit the KPgB in terrestrial sections. We have performed in-situ XRF measurements, using a Bruker Tracer IV-Geo spectrometer, on sediments from the Puig Pedrós Section (Trempe basin, Catalonia, Spain), where a relatively large amount of spherical particles had been previously found. Detailed geochemical data

(ICP-MS) from the spherules and from whole rock samples, as well as a long record of isotopes (C and O) obtained from edaphic nodules were available for the studied section. Although no iridium was detected in any of the samples investigated, several ICP-MS and isotopes results might provide an indication of the KPgB horizon: i) increased concentration of Ni and also Zn, Sn, Cr, As, Pb and Hf in the spherules, relative to the whole rock; ii) shift of stable isotopes from pedogenic nodules in the spherule-bearing interval; iii) increase of several trace elements in whole rock samples.

Here we show that the intensity of several pXRF peaks from trace elements like Zn, As, Ga or Rb correlate well with the ICP-MS data, thus suggesting that the portable XRF equipments may provide useful geochemical information in relation to the KPgB in distal non-marine settings. The limitations of the in-situ XRF measurements for this type of studies are also discussed.

P-19**Laser ablation ICP-MS study of trace elements from different deposit/mineralization types of molybdenite****JANA DURISOVA¹, MARTIN SVOJTKA, JAN PASAVA**¹ Institute of Geology of the CAS, Prague (Czech Republic)

An Element 2 high resolution ICP-MS coupled to a 213 nm Nd:YAG UP-213 laser ablation system was introduced to acquire molybdenite trace elements data. We analysed four different types of molybdenite associations from the Czech part of the Bohemian Massif (greisen-, gold-, base metal- and "barren granite"-related) and also the Almalyk porphyry-Cu-Mo(Au) deposit from Uzbekistan. The following isotopes were measured: (1) ⁷⁵As, ⁷⁷Se, ⁹⁰Zr, ⁹³Nb, ¹⁰⁷Ag, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁸²W, ¹⁸⁷Re, ¹⁹⁷Au, ²⁰⁸Pb and ²⁰⁹Bi in low mass resolution mode ($m/\Delta m = 300$), and (2) ⁵⁹Co, ⁶⁰Ni, ⁶³Cu and ⁶⁶Zn in medium mass resolution mode ($m/\Delta m = 4000$). Trace elements data except Zr, Nb and Re were calibrated against the synthetic polymetal sulphide MASS-1 using the isotope ³⁴S as an internal standard. Zr, Nb and Re were calibrated against the synthetic silicate glass standard NIST SRM 612. The isotope ¹⁸²W and its concentrations in the molybdenite samples obtained from the calibration with MASS-1 were used for internal standardisation.

Both external standards and molybdenite samples were analysed at identical conditions: a repetition rate

of 5 Hz, a laser fluence of 3-3.5 J/cm² and a beam size of 40-80 μ m depending on the grain size. The accuracy was monitored by the Sikhote-Alin meteorite and the NIST SRM 612 as no molybdenite reference material is available.

Our study showed that greisen-related molybdenite showed the highest mean value of W, As, Cu, Zn and Co, which are often related to a presence of nano- to micro-scale inclusions of various mineral phases (Fig.1). Gold-related molybdenite is characterized with the highest average values of Au, Ag, Bi, Se, Te and Sb, which are represented by numerous microinclusions of native bismuth, Au-Ag and various tellurides and selenides. Base metal-related molybdenite with its highest average Pb value contains abundant galena and/or anglesite (micro)inclusions. Granite-related molybdenites show the highest average Ni value. Porphyry-Cu-Mo(Au) related molybdenite from Almalyk deposit revealed the highest mean Re value (235.7 ppm) indicating dominant mantle source of Re.

P-20**Geochemical and mineralogical characters of the coastal plain sediments of the Arabian Gulf, Kuwait****ADEL AHMED ALY ELHABAB¹, IBRAHIM ADSANI**¹ College Technological Studies, Petroleum Engineering Department (Kuwait)

The present study deals with detailed geochemical and mineralogical studies of the coastal plain sediments were formed along the shoreline of the Arabian Gulf area, Kuwait. These deposits are mainly fluviomarine and beach sands.

The coastal plain deposits of the central Kuwait shoreline zone were found to consist of average medium-grained sand. The sand is composed, on average of about 90% sand, and the remains about 10% or less is mud, and has a unimodal distribution with a mode of medium sand (1-2 ϕ).

The sediments consists mainly quartz, Feldspar, clay minerals with carbonate minerals (detrital calcite and dolomite) and rock fragments (chert).

The mineralogy of the clay fractions of the sediments is dominated by illite, palygorskite, mixed layer illite-montmorillonite with minor amounts of chlorite and Kaolinite

Heavy minerals are concentrated in the very fine sand fraction and are dominated by opaque minerals,

and non-opaque minerals which represented by amphiboles, pyroxenes, epidotes, dolomite, zircon, tourmaline, rutile, garnet and other which represented by Staurolite, Kyanite, Andalusite and Sillimanite as a trace amounts.

Chemical analysis for the detrital amphibole grains from sandstone of coastal plain sediments shows the following features. The grains which have $(Na+K) < 0.50$ its composition ranges from actinolite to magnesio hornblende, but the grains which have $(Na+K) > 0.50$ its composition have wide variation and on the $(Na+K)-Al_{IV}$ diagram can be characterized two associations: Association 1 which characterized by low amount of Al_{IV} and low amount of $(Na+K)$, by comparing the chemical composition of this association and the chemical composition of amphibole grains from older basement rock, can be said, these associations may be derived from metamorphic source rocks and association 2 which characterized by high amount of Al_{IV} and low amount of $(Na+K)$, may be derived from volcanic source rocks.

P-21

Geochemical and mineralogical analysis of KupferschieferANNE RAHFELD¹, ROBERT MÖCKEL, JENS GUTZMER¹Helmholtz-Zentrum Dresden-Rossendorf, Freiberg (Germany)

Kupferschiefer, i.e. very fine-grained and disseminated polymetallic Cu-Ag ores of the extensive stratabound deposits of the Central European Copperbelt is well known for its mineralogical complexity and the challenges surrounding its characterization. It is marked by a combination of high metal sulfide contents (up to 25 wt%) and organic matter (up to 30 wt%) within a matrix predominantly composed of fine-grained clay and carbonate minerals. Conventional analytical procedures often yield unreliable results of this very complex raw material. Regardless, recent research into the hydrometallurgical and microbiological beneficiation of Kupferschiefer has raised the demand for supplying reliable quantitative data of the mineralogy and the geochemistry for both the raw material and process samples. A research project was thus initiated to establish a robust analytical procedure to quantify both mineralogical as well as geochemical attributes of Kupferschiefer-type ores. A combination of analytical techniques is employed for this purpose, including quantitative X-ray diffraction (QXRD), image analysis based on scanning electron microscopy/mineral liberation analysis (MLA), XRF, ICP-AES, and INAA. Method development was based on selected Kupferschiefer samples obtained from Sangerhausen (Germany) and Polkowice-Sieroszowice (Poland) deposits. QXRD by Rietveld refinement is particularly well-suited to determine the modal mineralogy of fine-grained samples. Five types of layer silicates were identified in Kupferschiefer samples. These are being characterized in detail in order to build crystal structure files needed to enable a full quantification of the minerals present. The necessary characterization

of this set of layer silicates has been inhibited by the presence of organic matter, requiring chemical pre-treatment of the raw material that is specifically developed for this purpose. SEM-based mineral liberation analysis (MLA) on grain mounts of crushed aliquots of the powder samples used for QXRD is used to verify mineral identification and to determine the amounts, liberation, and types of sulphide minerals contained in the samples. This technique is not suited to determine the abundance of the silicate minerals due to their fine-grained and intimately intergrown texture. Further obstacles, such as misidentification of disordered carbonate minerals by XRD or copper sulfides by MLA, are encountered often and can only be recognized and minimized by verifying results using multiple analytical methods. Independent observations from microscopy or bulk geochemistry by fusion XRF are useful in ensuring a high data quality and to test for consistency. Whole rock trace element data are acquired using INAA, XRF, and ICP-OES. While INAA can guarantee a full analysis without requiring a problematic digestion treatment, the procedure itself is not available for routine measurements. XRF analysis of pressed pellets has been inhibited by the variable content of organic material and matrix effects caused by high sulfide concentrations. ICP-AES/MS analysis is considered to be the most appropriate technique in this case. Different combinations of hydrogen peroxide, nitric acid, and perchloric acid digestion techniques are tested to identify an optimal procedure for the acid digestion of the diverse sulfide compounds as well as the organic matter contained in Kupferschiefer.

P-22

In situ trace element analysis of gem opals from Dubník (Slovakia): Comparison of LA-ICP-MS and ICP-MS dataLADISLAV STRNAD¹, NIKOLETA ČIMOVÁ², ONDŘEJ ŠEBEK¹¹Faculty of Science, Charles University in Prague, Prague (Czech Republic)²Czech Geological Survey, Prague (Czech Republic)

Samples of gem opals from the historically famous Dubník locality (Slovakia) were analysed for major elements by wet analysis and for trace elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and solution ICP-MS. The sample introduction system and calibration and correction strategy closely followed those described by Strnad *et al.* (2005). The study focuses on the geochemical relationships between various types of opals from Dubník and compares them with data from other localities around the world. The Dubník opal district is located in Neogene calc-alkaline volcanics and extraction of opals has been documented here since the Roman Empire.

Major element analyses showed that opals are essentially pure SiO₂ (77 – 92 wt%). The other major constituents forming opals are Al₂O₃ (0.25 – 1.34 wt%), CaO (0.12 - 0.46 wt%), K₂O (0.04 - 0.19 wt%) and MgO (0.02 - 0.15 wt%). The H₂O content varied

significantly from 6 to 21 wt% for all the samples. LA-ICP-MS analyses showed substantial dispersion of the data for all the samples, e.g. in the total concentrations of REE (Σ REE from 0.28 to 28.1 mg/kg), similar to the data obtained for solution ICP-MS (Σ REE from 0.35 to 24.9 mg/kg). On the other hand, the REE distribution patterns displayed very flat trends and very weak negative Eu anomalies. The replicate laser ablation analyses ($n = 5$) for a single sample yield a precision (given as one relative standard deviation, RSD) 2 – 21 % for most REE. Comparisons of the results (from both ICP-based techniques) for the other trace elements are more complicated and indicate elemental heterogeneity of opals within a single sample. However, the highest and very variable concentrations corresponded to Ba (2 – 119 mg/kg), Rb (0.2 – 42 mg/kg), Sr (1 – 39 mg/kg), Mn (0.5 – 30 mg/kg) and Ni (2 – 17 mg/kg). Refractory elements (e.g. U, Th, Zr, Hf) are present in very low concentrations and/or lie below the detection limit.

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P-23**Reference materials and an international proficiency testing programme for microanalytical laboratories****JENNIFER M COOK¹, DOUGLAS L MILES²**¹ British Geological Survey, Keyworth, Nottingham (UK)² IAGeo Limited, Keyworth, Nottingham (UK)

Ever since the ground breaking work of Fairbairn *et al.*¹, which highlighted the large scatter of values for the elemental composition of two silicate rocks (G1 and W1) obtained by different analytical techniques in different laboratories, interlaboratory collaborative analytical programmes have become widely recognised as valuable tools in our continuing quest to understand and improve the performance of geoanalytical methods. Modern microanalytical techniques such as laser ablation (LA-ICP-MS), electron probe microanalysis, scanning electron microscopy and micro-XRF pose particular additional problems because of the high spatial resolution required and the sometimes poorly understood excitation and detection processes involved.

Building on the success of its GeoPT proficiency testing scheme² that has been running for twenty years and currently involves over a hundred laboratories worldwide, the International Association of Geoanalysts (IAG) in close collaboration with the United States Geological Survey has developed G-Probe, a proficiency testing programme for microanalysis. In parallel, a growing range of reference materials is being developed specifically to serve the needs of laboratories using microanalytical methods.

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P-24**Long-term laser ablation system stage return accuracy: Sub-micron performance in real applications****ROB HUTCHINSON¹, DAVID WRAY, KATHERINE MCLACHLIN, CIARAN O'CONNOR, LEIF SUMMERFIELD, JAY WILKINS, ERIK LARSEN**¹ Electro Scientific Industries, Europe Ltd., Huntington, (UK)

Mineral grain analysis, in particular zircon analysis, is a common application for LA-ICP-MS and the theory and methodology are well established. The high throughput nature of the analysis requires the accuracy of manual ablation and the speed of hands-off automated analysis, however, to run in this manner for hours or even days significant confidence is needed that all ablations will run in the precise locations intended. An error of a few microns can

result in ablation occurring in the grain rim, which is frequently a difference age to the core, ruining the analysis and wasting a valuable sample. ESI has met this challenge through evolution in sample chamber and stage design that have led to improvements in short and long term stage accuracy. The most significant of these is ImageLock, a software-based feature which has been shown in controlled conditions to give long term stage return accuracy of

P-25

Challenges and solutions on the major and trace element analysis of Eudialyte group minerals with the electron microprobe

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The accurate quantification of the chemical composition of eudialyte group minerals (EGM), one of the most promising sources for future REE supply, is complicated by both mineralogical and X-ray-specific challenges. These include: 1) structural and chemical variability of EGM composition (e.g., Johnsen *et al.* 2003, Rastsvetaeva 2007, Schilling *et al.* 2007); 2) mutual interferences of X-ray lines from major and trace elements, in particular REEs (Pyle *et al.* 2002) [4]; 3) the diffusive volatility of light anions as F and Cl and cations such as K and Na; 4) particular instability of EGM under the electron beam.

A novel analytical approach has been developed to account for the above-mentioned analytical challenges. The present study focussed on the optimization of beam conditions in order to minimize

the effects of instability of EGM under the electron beam and to develop a robust procedure for the correction of mutual interferences. Additionally, loss on ignition and differential scanning calorimetry data has been applied to constrain the content and composition of volatiles in the EGM structure. The influence of the electron beam on the structure of EGM has been explored with Raman spectroscopy. All correction for the overlapping of X-ray lines is processed offline. For comparison a subset of samples was analysed with LA-ICP-MS. The results demonstrate that the above-mentioned parameters need to be considered and carefully optimized to perform accurate quantitative analyses on the chemical composition of EGM with the electron microprobe.

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A novel approach for efficient identification and accurate chemical characterisation of platinum-group minerals by combining Electron Probe Microanalysis and Mineral Liberation Analysis

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The identification and accurate characterisation of platinum-group minerals (PGMs) is usually a very cumbersome procedure due to their small grain size (typically below 10 µm) and inconspicuous appearance under reflected light. A novel strategy for finding PGMs and quantifying their composition was developed. It combines SEM-based automated mineralogy, in this study mineral liberation analyser (MLA) Quanta 650F by FEI, a point logging system (JEOL) and a FE-EPMA (JEOL JXA-8530F). Thin sections from a layered intrusion (UG2) in the Bushveld Complex and from two Uralian-Alaskan-type complexes in the Ural Mountains, Russia, were investigated as case studies.

As a first step, the PGMs are identified using the MLA. Grains identified as PGMs are then marked and coordinates recorded and transferred to the EPMA. Case studies illustrate that by introducing MLA for the efficient and largely automated identification of PGM grains in polished thin sections, up to 20 times more PGM grains were identified, whilst shortening

time needed and avoiding the effects of human error invariably associated with reflected light microscopy. This is mainly due to the facts that (a) PGM with grain sizes < 5µm are reliably identified and (b) PGM and closely associated base metal sulfides and sulfosalts are well differentiated with the MLA. The analysis of PGMs by EPMA requires considerable effort due to the often significant overlaps between the X-ray spectra of almost all platinum-group and associated elements (e.g. OsMβ on IrMα and AuMβ on HgMα). X-ray lines suitable for quantitative analysis need to be carefully selected. As peak overlaps cannot be avoided completely, an offline overlap correction based on weight proportions has been developed. Considerable variations in the repeatedly determined overlap factors illustrate the need for a re-determination of the overlap factors with each calibration. Results obtained with the procedure proposed in this study attain acceptable totals and atomic proportions, indicating that the applied corrections are appropriate.

P-27**Determination of rare earth elements in geological samples with radio-frequency glow discharge mass spectrometer****HYUNG SEON SHIN¹, CHAN-SOO PARK¹, YOUNGWOON KIL¹, JAE-YEOL YANG¹, JAESIK YOON¹**¹Korea Basic Science Institute (South Korea)

The glow discharge (GD) method has been widely applied in the field of bulk elemental composition, depth profiling, and isotopic composition for metals, metal-alloys and semiconductors. Typically, glow discharge (dc-GD) is formed electrically conductive or semiconductive materials. Therefore, it has a limitation for analyzing a non-conductive samples. It is required a chemical modification of nonconducting materials in glow discharge method.

The adaptation of radio-frequency (rf) glow discharge has an advantage of no chemical modification of nonconducting materials.

In this study, rf-glow discharge mass spectrometer (rf-GD-SFMS) was used for determination of rare

earth elements (REEs) in geological samples-such as rock and, sediments.

About 2.5 g powder samples are mixed with 5 g of mixed fusion flux (lithium metaborate (LiBO₂) + lithium tetraborate (Li₂B₄O₇), then, made glass beads by an automatic fusion machine.

The glass bead samples were analyzed with rf GD-SFMS (GD90). The recoveries of REEs in standard reference materials, BHVO-2, SGD were about 80 %~120 % . Compared with ICP-MS method (acid digestion), an errors in GD MS were slightly higher than that of ICP-MS.

P-28**Certified reference materials of lithium ore produced at Central Geological Laboratory of Mongolia****ARIUNBAT AASUREN¹, UNURMAA GOMBOJAV¹, OYUNTUNGALAG URJIN¹**¹Central Geological Laboratory, Ulaanbaatar (Mongolia)

Based on increasing demand of lithium in high-tech technologies and feasibility study, Central Geological Laboratory of Mongolia (CGL) had produced a certified reference material of lithium ore "CGL 128 LiH" within 2012-2014 in accordance with relevant standards (ISO Guide 30 series).

Bulk material of around 115 kg was collected from the Arban tungsten-lithium deposit located in territory of Erdenetsagaan soum, Sukhbaatar province (Eastern Mongolia) for further processing. Short-term and long-term stability studies and homogeneity study were passed.

An interlaboratory approach with 14 qualified participating laboratories from 9 countries was selected to obtain a reliable base of data for assignment of the certified values. A nested design was chosen for maximum information output. The traceability was established to the existing CRM "NCS. DC 86303 Lithium ore", China. Based on statistical processing of certification data, certified values were assigned for 18 elements and information values for 38 elements.

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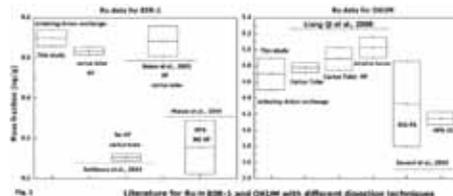
Determination of Ru in OKUM and BIR-1 with sintering-anion exchange

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The application of wet acid treatment is limited when determination of highly resistant metals i.e. Ru, Rh, Os, and Ir are concerned because these resist the treatment of mineral acid and aqua regia. Decomposition of silicates with HF acid is normally required for releasing precious metals occluded within the grains with microwave and high pressure systems [1].

Alkaline fusions are an effective way for dissolution of acid resistant metals Ru, Rh, Os and Ir. We aim to further modify and develop the method initially used for Re determination [2] with sintering-anion exchange and extend to determination of Ru hosted in silicate phases in OKUM and BIR-1. For that purpose replicates of OKUM and BIR-1 (0.5 g) have been digested with sintering and after centrifugation, supernatant and hydroxides have been separated and dissolved in dilute and concentrated HCl. To each of the phases PGE isotopes enriched spike was added as equilibration of spike before centrifugation was

not established. As in alkaline fusion, during Na₂O₂ sintering, sodium ruthenate (Na₂RuO₄) is formed and is converted to stable RuOHCl₅²⁻ and Ru₂OCl₁₀⁴⁻ complexes after acidifying the solutions [3]. Thus anionic chloro complexes were separated with anion exchange column (AG1X8). Preconcentration is done with anion exchange chromatography using 8 mol/l, 12 mol/l and 14 mol/l HNO₃. Measurements were performed with Agilent 8800 ICP-MS/MS using different gas modes. Preliminary data obtained is in good agreement with literature values [4-7] as shown in Fig. 1. Developed method is being extended to determination of ultra-trace concentration of PGE in reference materials.



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P-30

Determination of Ru, Pd, Rh and Au in MUH-1 reference material with sintering-Te-co-precipitation with ID-ICP-MS

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As for many isotope systems, matrix matched certified reference materials (CRM) of real samples are very rare. Solutions of known isotopic composition are used for quality assurance and quality control but matrix matched reference materials are needed for evaluation of measurement uncertainties. MUH-1, a depleted harzburgite (Kraubath, Austria) has been prepared and is already certified for major and trace elements by an inter-laboratory certification (ILC) process lead by the International Association of Geoanalysts (IAG). PGE determination in geological materials is difficult due to trace abundances, heterogeneous distributions and due to lack of universal sample digestion technique for all PGEs. Common methods are alkaline fusion, NiS fire assay with tellurium co-precipitation and acid digestions with carius tubes and HPA etc.

In alkaline fusion samples are fused with the flux above its melting point using corundum or zirconium crucibles. We aim to test the sintering of sample with Na₂O₂ flux below its melting point using glassy carbon crucibles. Pre-concentration has been achieved through tellurium co-precipitation. 0.5 g test portions of MUH-1 were digested and spiked with PGE enriched isotopes. SnCl₂ and Te were added for precipitation of PGE. Te-PGE precipitates were dried and dissolved with aqua regia and 0.1 mol/l HCl. Measurements were performed with ICP-MS/MS Agilent 8800. Preliminary data is in good agreement with mean of ILC values. High blanks are of concerns which are being improved in further PGE studies.

Ru, Pd, Rh, and Au data (ng/g) with sintering-Te-co-precipitation				
Analyte	Ru	Pd	Rh	Au
Mean (ng/g)	9.84	10.7	0.79	6.65
RSD	9%	24%	10%	8%
Blanks	0.03	0.41	0.26	0.29
ILC mean	8.08	8.90	1.10	6.24

Acknowledgement: Thomas Meisel (for provision of preliminary MUH-1 ILC data 2015).

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U-Pb and Lu-Hf calibration of the new LA-ICP-MS Multilab at Rio de Janeiro State University

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A new Finnigan NEPTUNE MC-ICP-MS coupled with a laser ablations system has been installed and is in full operation at the Multilab of the Rio de Janeiro State University. This in-situ technique allows determination of small volume samples and low concentrations of U and Pb using an ion detection system with very high sensitivity.

Zircon analyses of U-Pb elements and isotopes are carried out simultaneously on and collectors are comprised of the nine faraday cups and four CDD and three ion multiplier. The organization of the machine allows the detection of the ²⁰²Hg, the (²⁰⁴Pb + ²⁰⁴) Hg masses and ²⁰⁶Pb and ²⁰⁷Pb isotopes within the ion counters. The collector configuration is: ²⁰²Hg (IC-4), ²⁰⁴Pb (IC-05), ²⁰⁶Pb (IC-3), ²⁰⁷Pb (IC-2) and ²⁰⁸Pb (IC-1). The ²³⁸U abundance is measured in Faraday cup H4 and ²³²Th in H3 faraday cup.

Samples are ablated by laser pulses at 8-10 Hz repetition rate, 40s of ablation with a spot size of 25-30µm and power of 50-55%. Helium flux (0.755 ml) is calibrated together the sample gas (0.800 ml Ar). After the acquisition raw data are processed offline using an Excel spreadsheet table for blank and GJ-1 zircon standard corrections. Initial data on GJ-1 zircon yielded ²⁰⁷Pb/²⁰⁶Pb values of 0.05967 ± 0.0004 (true value 0.06013); ²⁰⁶Pb/²³⁸U values of 0.09570 ± 0.0023 (true value 0.0975); ²⁰⁷Pb/²³⁵U values of 0.8032 ± 0.02 (true value 0.8085). These values yielded an average age of 603 ± 5.7 Ma similar to the true value.

For the Lu-Hf technique we analyzed the same zircon grains dated for U-Pb as described above, using the same epoxy mount and CL images. The collectors were positioned as follows: in the central collector (¹⁷⁶Hf), mass in collectors H1 (¹⁷⁷Hf), H2 (¹⁷⁸Hf), H3 (¹⁷⁹Hf) and H4 (¹⁸¹Ta); L1 (¹⁷⁵Lu), L2 (¹⁷⁴Hf), L3 (¹⁷³Yb) and L4 (¹⁷¹Yb). The used reference materials are zircon GJ-1, 91500 and Mud Tank.

Isotope data are acquired using static mode and isotope abundances are corrected for blank values. Laser operating conditions include output power 5 to 6.5 J/cm², shot repetition rate=10 Hz and laser spot of 40 µm. Gas input flow (Ar) of 15 l/min, auxiliary flow (Ar) 0.8 l/min, sample gas flow 0.80 l/min (Ar) in the MC-ICP-MS and carrier He flow 0.20+0.60 l/min in the Laser. Data are normalized to ¹⁷⁹Hf/¹⁷⁷Hf (true value 0.7325). Isotopic ratios and inter-element fractionation are evaluated offline by interspersing the GJ-1 standard zircon. To correct the isobaric interferences of Lu and Yb isotopes of mass 176, the isotopes ¹⁷¹Yb, ¹⁷³Yb and ¹⁷⁵Lu are simultaneously monitored during each analysis. The ¹⁷⁶Lu and ¹⁷⁶Yb are calculated using a ¹⁷⁶Lu/¹⁷⁵Lu (true value 0.026549) and a ¹⁷³Yb/¹⁷¹Yb (true value 1.123456). During the course of the analyses the ¹⁷⁶Hf/¹⁷⁷Hf GJ-1 standard was 0.281994±5 (n=50, 2SD), which is almost identical to the recommended value in the literature of 0.282000±5. To evaluate the accuracy and precision of the laser-ablation results, we have analyzed two zircon standards, 91500 and Mudtank, during the analyses, which ¹⁷⁶Hf/¹⁷⁷Hf results are 0.282311±80 and 0.282507±51 respectively.

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Pb isotopic measurements in NIST 612 by LA-ICP-MS (Neptune)

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Lead isotopic composition is widely used in geology and environmental research. The increasingly proliferation of analytical techniques capable of in situ microanalysis of isotope composition has some obstacles, such as elemental fractionation during laser ablation and mass discrimination during the ion transfer from the ion source to detectors in the mass spectrometer. MC-ICPMS technique combines advantages of both TIMS (multicollector) and ICP (high ionization efficiency) and when used with laser ablation in situ sampling could obtain lead isotope composition precisely as isotope dilution ID-TIMS. This contribution aims to present the initial results of Pb isotopes analysis realized on NIST 610 reference material and to discuss in order to define the correction factor for the mass fractionation observed in our laboratory compared with published results of this standard in other laboratories.

The collectors of the spectrometer settled at Multilab/Uerj are comprised of the nine faraday cups and four CDD and three ion multiplier. The U-Th-Pb isotopes systematic includes the measurement of ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th and ²³⁸U. It is important to measure ²⁰²Hg simultaneously with the Pb isotopes in order to monitor and correct for the isobaric interference of ²⁰⁴Hg on ²⁰⁴Pb. In this way, the collector configuration is: ²⁰²Hg (IC-4), ²⁰⁴Pb (IC-05), ²⁰⁶Pb (IC-3), ²⁰⁷Pb (IC-2); ²⁰⁸Pb (IC-1); ²³²Th (H2); and ²³⁸U (H4).

We ablated 272 spots by laser pulses at a 8-10 Hz repetition rate, during 40s of ablation with a spot size

of 25-30µm and power of about 50-55%. Helium flux (0.755 ml) has to be calibrated together the sample gas (0.800 ml Ar) in the plasma to obtain the higher and more stable signal. No internal mass fractionation controller was used. Isotopic ratios, blank, 202 correction and inter-element fractionation were evaluated offline by comparing with NIST reference material true values from literature. Results of NIST 612 reference material yielded values (volts) from 0.00000781 to 0.00000727 ($\Sigma = 0.00000739$) of ²⁰²Hg; 0.0000486 to 0.000427 ($\Sigma = 0.0000447$) of ²⁰⁴(Hg+Pb); 0.00103 to 0.00073 ($\Sigma = 0.00091$) of ²⁰⁶Pb; 0.000930 to 0.000710 ($\Sigma = 0.000759$) of ²⁰⁷Pb; 0.00204 to 0.00157 ($\Sigma = 0.000183$) of ²⁰⁸Pb. For ²³²Th and ²³⁸U measurements on faraday cups the values are 0.00270 to 0.00245 V ($\Sigma = 0.00250$) and 0.000384 to 0.00300 V ($\Sigma = 0.000360$), respectively.

The averages for isotope ratios are: ²⁰⁶Pb/²⁰⁴Pb = 21.7913, ²⁰⁷Pb/²⁰⁴Pb = 20.3511, ²⁰⁸Pb/²⁰⁴Pb = 44.5952, and ²⁰⁷Pb/²⁰⁶Pb = 0.74506. The true values, according to literature, are: 17.047, 15.509, 36.976 and 1.0991, respectively. The procedure to correct this mass fractionation is obtained applying the corrector factor. These reported values (true values) are compared with the data here obtained indicated the following fractionation factor: ²⁰⁶Pb/²⁰⁴Pb = 1.2826, ²⁰⁷Pb/²⁰⁴Pb = 1.3168, ²⁰⁸Pb/²⁰⁴Pb = 1.2105, and ²⁰⁷Pb/²⁰⁶Pb = 0.6778. The Pb isotope values here obtained are coherent with the results reported in the literature. The results are statically accurate using the multicollectors.

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Quantification of trace and rare earth elements in samples of banded iron formations of the Quadrilátero Ferrífero, Brazil, among the production of reference material

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Banded iron formations are Precambrian sedimentary rocks of chemical origin, which resulted in itabirites after exposure to metamorphic conditions. Due to the significant percentage of iron present in the form of hematite and magnetite, these rocks are important economic sources of iron ore. Aiming to elaborate reference materials for this type of matrix, about 15 kg of three samples of different types of iron formation were properly crushed, pulverized and split, and then subjected to sufficient homogeneity test. In order to achieve that, standardized analytical procedures were performed, such as simple titration, Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and X-Ray Fluorescence Spectrometry, which allowed to determine the composition of the major elements in the samples (SiO₂, Al₂O₃, Fe₂O₃, FeO, CaO, MgO, TiO₂, MnO, P) and Lost on Ignition (LOI). The results were obtained under repeatability conditions, in which the same operator in the same laboratory using the same methods and the same equipment performed the analyses in a minimum period of time for which the variability in the results was not resultant from the accuracy of the methods adopted, but essentially

from material homogeneity. The procedures were shown to be appropriate for the intended use and allowed to establish, according to a significance level of 0.05, the sufficient homogeneity for the material analyzed, and enabled the later stage of development of methods for the determination of trace elements. The small mass fraction of trace elements, including rare earth elements, prevents their determination from conventional dissolution methods, which lack in reference materials with certificated values for rare earth elements to validate it. In this study, the analytical dissolution procedure tested used hydrofluoric, nitric, hydrochloric and perchloric acids and the quantification of these elements was performed by ICP-MS. All results were validated by comparison with the values published in the literature for IF-G and BRP-1 reference materials, which ensured the metrological traceability of the data. The results allow the production of internal reference material (in-house), which enables, in turn, the analytical quality control of the data generated for banded iron formation matrices. Further step in this work is to set off an interlaboratorial programme.

Sample	SiO2 %	Al2O3 %	P %	MnO %	CaO %	TiO2 %	MgO %	Fe2O3 %	FeO %	LOI %
FZ-JF-07	55,71	0,14	<0.004	0,05	0,04	0,01	0,05	48,13	0,54	0,07
FZ-HE-08	1,17	0,49	0,013	0,04	0,03	0,02	0,03	97,82	0,33	0,16
FZ-JFR-03	25,28	0,38	<0.004	0,41	0,01	0,01	0,03	73,87	0,08	0,29

	V mg/kg	Cr mg/kg	Co mg/kg	Ni mg/kg	Ba mg/kg	La mg/kg	Ce mg/kg	Pr mg/kg	Nd mg/kg	Sm mg/kg
FZ-JF-07	9,38	10,2	0,70	3,16	4,72	0,58	1,03	0,11	0,49	0,14
FZ-HE-08	21,8	20,8	0,75	4,03	5,49	1,61	2,82	0,41	1,85	0,42
FZ-JFR-03	3,63	3,59	7,98	21,8	76,8	4,40	4,30	1,65	7,28	1,10

	Eu mg/kg	Gd mg/kg	Tb mg/kg	Dy mg/kg	Ho mg/kg	Er mg/kg	Tm mg/kg	Yb mg/kg	Lu mg/kg	Hf mg/kg
FZ-JF-07	0,05	0,20	0,03	0,24	0,06	0,20	0,03	0,21	0,04	0,03
FZ-HE-08	0,13	0,46	0,07	0,43	0,10	0,29	0,04	0,26	0,05	0,10
FZ-JFR-03	0,26	0,71	0,10	0,58	0,12	0,38	0,06	0,38	0,07	0,03

P-34

Concentration of metals and semi-metals in black shales: A new sequential protocol

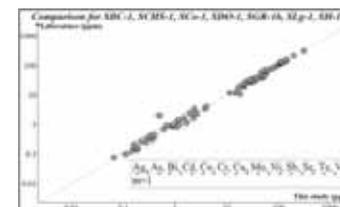
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We have developed a new sequential extraction technique for determining metals and semi-metals contents of carbon-rich rocks. Six international geological reference materials (SGR-1b; SCo-1; SBC-1; SDO-1; SCHS-1 and SLg-1) and our in-house reference material, black shale (SH-1), were selected in order to test the method. The whole rock values for these reference materials agree with the values available from the literature (Figure 1). In addition with this new protocol it is possible to determine the partitioning of elements among the components of black shales. The protocol consists of four main steps: 1) diluted HCl acid digestion (fulvic acid extraction), 2) NaOH digestion (humic acid extraction), 3) aqua regia digestion (sulphides phase dissolution) and 4) hydrofluoric acid digestion (silicates dissolution). The solutions from each step were analysed by ICP-MS. Satisfying accuracy and high precision was found in the results. The results were compared with literature when available and the modified Horwitz function was used to evaluate the accuracy of the technique. In contrast to traditional acids attack that commonly

involve aqua regia and hydrofluoric acid, this new 4-steps sequential extraction methodology allows the determination of moderately volatile elements by early extraction at low temperature from the organic material in colloidal phases, followed by aqua regia and HF digestion. The 4-steps extraction shows better recovery than classical aqua regia / HF digestion. Furthermore, this method of analysis permits us to determine to which component (calcareous-biogenic, sulfur or oxide-siliceous-rich phases) the metals and semi-metals are associated with. Regarding the seven studied shales, we notice that each sample has a different partitioning of metals and semi-metals. This feature results from their contrasting syn-sedimentary, diagenetic and post-diagenetic conditions. However, some elements have more consistent behaviour. For instance, Cr, V and U are hosted by silicates and oxides. Other elements such as Ni, Ag, Cu, Te, Co, As and Pb are hosted mainly by sulfides, elements such as Bi, Cd, Mo and Se suggest a large contribution from organic material.

Figure 1: Comparison between concentrations obtained in this study with literature for Ag, As, Bi, Cd, Co, Cr, Cu, Mo, Ni, Sb, Se, Te, V in SBC-1, SCHS-1, SCo-1, SDO-1, SGR-1b, SLg-1 and SH-1.



P-35 10 years GeoReM database

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In 2005, Jochum *et al.* (2005) developed a geochemical database of reference materials (RMs) of geologic and environmental interest, called GeoReM, which is accessible to the scientific community on the internet (<http://georem.mpch-mainz.gwdg.de>). Geochemists can easily have access to information about those RMs that are of particular importance to their research (Jochum and Enzweiler 2014). The total number of RMs in GeoReM continually increased: in October 2005 (Application Version 1) about 750 RMs were available, Application Version 18 (January 2015) contains now more than 3100 RMs. The number of analyses and papers also increased substantially (analyses: 6000 (2005), 34200 (2015); publications: 650 (2005), 7600 (2015)). Whereas in 2005 only

three different ways of enquiry were possible, the number of search strategies in 2015 is six. Currently, about 2000 scientists from more than 100 countries use the database every month. New developments are in progress in order to improve the usability of GeoReM. Examples are the link to recent literature highlights on RMs and the optional presentation of analytical data by atomic or alphabetical order. The database is useful to determine reliable reference values of RMs, where no or only few certified values exist. This was done to determine reference values and their uncertainties following ISO guidelines for the NIST SRM 610x glasses (Jochum *et al.* 2011) and recently for the 20 most frequently requested rock RMs (Jochum *et al.* 2015).

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P-36 Novel dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry for the determination of trace noble metals in geological samples

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The pre-concentration procedure is necessary during the analysis of trace noble metals in geological samples. For the traditional methods such as foam sorption, liquid-liquid extraction and single drop microextraction, disadvantages such as large usage of harmful solvents or time-consuming could not be avoided. Assadi and co-workers developed a new microextraction method called dispersive liquid-liquid microextraction (DLLME). (Rezaee *et al.* 2006) In this method, the appropriate mixture of extraction and disperser solvents is rapidly injected into aqueous samples containing analytes. By this way, a cloudy solution will formed due to the dispersion of droplets of the extraction solvent in the sample solution. After centrifugation, the extraction droplets are collected from the bottom of tube and are ready for instrumental analysis. The features of DLLME include low cost, use of minimized toxic organic solvents, rapidity, high enrichment factor and selectivity. (Shamsipur and Ramezani 2008) In addition, it is very suitable to combine this miniaturized sample pre-treatment technique with microamount sample analysis technique of graphite furnace atomic absorption spectrometry (GFAAS).

In this study, a modified DLLME method was developed and applied for the determination of trace noble metals in geological samples. The "light" and harmless solvents were chosen as both extraction and disperser solvents. The fine droplets of extracted solution came out at the top of solution by adding more water into the solution. Then, the extracted solution could be easily transferred into GFAAS by a injection for analysis. For the gold analysis, tributyl phosphate and ethanol were selected as extraction and disperser solvents, respectively. For the silver analysis, octanol, diphenyl thiourea ethanol and ethanol were used as extraction solvent, complexant agent and disperser solvent in sequence. It was found that the sensitivities of GFAAS combined with this modified DLLME method were more than 60 times higher than those of GFAAS without pre-concentration. This method had been successfully applied to determine trace amounts of both gold and silver in Chinese geological samples.

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Evaluation of whole-rock nano-particle pressed powder tablets for lithium and boron isotope analysis

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In this contribution we present continuing evaluation of a new approach to obtain reliable Li and B isotope compositions of whole-rock samples on a more routine basis. Although the sample preparation is not trivial, it has the promise of being accessible due to the whole-rock sample not having to be dissolved and chemically processed prior to analysis.

A recently established method allows the processing of whole-rock samples to yield nano-particle pressed powder tablets suitable for successful elemental analysis by LA-ICP-MS (Garbe-Schönberg and Müller 2014). A selection of reference materials (BIR-1, BHVO-2, UB-N, and SCOL) spanning a large range in Li and B concentrations and isotope compositions (Li: 1.6-27ppm, -3 to 4.9‰ $\delta^7\text{Li}$; B: 0.3-140ppm, -0.7 to 13.1‰ $\delta^{11}\text{B}$) were prepared as such nano-particle pressed powder tablets. These were analysed by LA-MC-ICP-MS for Li and B isotope compositions, using a NewWave solid-state UP193 coupled to a NuPlasma HR operating at 6kV and fitted with a so-called low mass, high abundance skimmer cone. Instrumental protocols build on previous success with similar analysis of natural or synthetic glass samples (Le Roux 2010, Le Roux *et al.* 2004). However, in this study we used 100 μm spot analyses of 60 second duration with pre-ablation (120 μm spot, 10 seconds) and not trenches as in the previous studies (Le Roux 2010, Le Roux *et al.* 2004).

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Preliminary results indicate sufficient sensitivity (0.3-0.6V total B) for meaningful B isotope analysis using faraday detectors. Repeat spot analyses distributed across these nano-particle pressed powder tablets show B isotopic homogeneity at the external 2σ reproducibility level of this method (± 0.2 -0.5‰). Using BHVO-2 as bracketing standard, geologically meaningful results are obtained for BIR-1 (-1.11 \pm 0.68 $\delta^{11}\text{B}$). At present, B isotope analysis of UB-N yields precise but significantly inaccurate $\delta^{11}\text{B}$ values. The B content of UB-N is much higher than BHVO-2 (140ppm vs ± 3 ppm), and a bracketing standard of similar B concentration might be required. Alternatively UB-N is a serpentinite with significant water-soaking minerals which might have been compositionally affected by the wet-milling process, even-though ultra-pure, low-boron water was used.

Results of the evaluation of these nano-particle powder tablets for similar Li isotope analysis by LA-MC-ICP-MS indicate significantly lower sensitivity ($\pm 0.25\text{V}$ total Li on BHVO-2 with 5ppm Li). Although still being evaluated, it is likely that Li isotope analysis of these nano-particle powder tablets by LA-MC-ICP-MS will only be possible using a Faraday-ion counter configuration as is the case presently glass samples (Le Roux 2010).

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Microelements' determination in rocks by ICP-MS: problems of routine analysis

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ICP MS is widely applied method for rocks microelement analysis of after samples acid decomposition. Nevertheless the problem of incomplete rocks decomposition remains relevant till now [Navarro *et al.* 2008, Fedyunina *et al.* 2012, Cotta and Enzweiler 2010, Hu *et al.* 2010]. The role of individual acids is not entirely clear at digestion of different minerals constituting the rock. There are not well studied mechanisms of the stable minerals decomposition, such as zircon, tourmaline, chromite, spinel, garnet, sphene, rutile, and others that may contain a significant amount of the microelements to be determined. There is not full understanding of the factors governing the processes of formation and destruction of complexes and insoluble phases over acid sample treatment. The problem of analytical results accuracy control for routine geological samples associated with a variety of mineral and chemical rocks composition and difficult to implement, especially when their petrographic description is not very accurate.

This work presents developed procedure for rock digestion and their application to routine analysis by high resolution ICP MS. The influence of the mixture $\text{HF-NH}_4\text{F-HNO}_3$ on Li, Be, Sc, V, Cr, Co, Ni, Cu, Ga,

Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, REE, Hf, Ta, W, Tl, Pb, Th, U determination in different types of rocks after bomb digestion is investigated. At the content of the fluoride ion (in terms of hydrofluoric acid) in the mixture to decompose more than 35% decomposition of all studied rocks types, including those containing stable minerals, is completed for 18-20 hours at a temperature above 190°C. The developed method applied for the standard samples analysis of basalt BCR-1 and BIR-1, shale SDC-1 and SBC-1, granite G-2, rhyolite RGM-1, granodiorite GSP-1 (USGS); the Russian garnet-biotite standard samples of plagioclase GBPg-1 (more than 2% garnet) and granite SG-1A (up to 3% of accessory minerals); the candidates standard samples of trachyandesite T-and and rhyolite, and RhT (Central Geological Laboratory, Mongolia). The accuracy of analysis is confirmed by the results of regular participation in the programmes of International proficiency testing scheme for analytical geochemistry labs (GeoPT27-35). XRF is used to assess the reliability of the routine samples analysis results. There were controlled elements, which are characteristic for the most resistant accessory minerals - V, Cr, Ni, Sr, Y, Zr, Nb, Ba. Differences in results, obtained by ICP MS and XRF for the same elements, were not exceeded 10% rel.

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LA-ICP-MS analysis of massive sulfides: progress towards a new calibration material

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Chalcophile elements which include base metals (e.g. Ni, Cu, Zn, Pb), traces metals (e.g. Cd, Co, Se, Te, Sb, In) and precious / ultra-traces metals (e.g. Au, Ag, PGEs) are commonly controlled by sulfides minerals (e.g. chalcopyrite, pentlandite, pyrrothite, sphalerite) in different geological context (high temperature-magmatic, hydrothermal, sedimentary). The sulfides minerals are therefore of economic importance and also important in understanding the geochemical cycle of these elements. Zonation and heterogeneous distribution of the elements are common in sulfides thus accurate in-situ determination is necessary. The use of LA-ICP-MS has gained popularity over the years; thanks to the instrumental flexibility and capacity to promptly analyze the almost entire periodic table at micrometer-scale size, with the ability to reach low (sub-ppm) limits of detection.

Matrix-matched reference material (RM) are recommended to calibrate LA-ICP-MS (Sylvester, 2008) but a noticeable constrain is the availability of such RM. Producing homogeneous RMs at micro-scale is challenging e.g. PGEs are known to form discrete mineral phases (PGMs) which segregated from sulfide melt at high temperature, resulting in heterogeneous, useless RM. As well, volatiles elements such as As, Se and Os can be lost during sample preparation. The commercially available RMs are limited; MASS-1 (USGS) is a pressed-pellet produced by chemical precipitation (Wilson *et al.*, 2002). The pellet has a high water and sodium content, thus it is a weak matrix-matched RMs. Moreover, the chemical composition is incomplete e.g. Ru, Pd, Re, Os were omitted. Consequently, most laboratories interested in LA-ICP-MS sulfide analysis produce their own in-house

RMs. Matrix-matched RM are difficult to produce, and their small size (<1g) limits their characterization by external methods, and distribution to other laboratories is not an option (e.g. Wohlgemuth-Ueberwasser *et al.*, 2007; Mungall and Brenan, 2014). Larger (c.a. 5g) samples were prepared but high fluxer (Li/B) to sample ratios (1:10) were used and fusion in Pt-Au crucible was necessary (Danyushevsky *et al.*, 2011). Heterogeneous distribution of Se, Tl, Pt and Au was reported. We are working on a new technique to produce calibration material for LA-ICP-MS, using natural powdered samples and have made serious progresses. The final RM should be composed of major elements: S (36%), Fe (48%), Ni (7.5%) and Cu (1.1%) thus suitable to calibrate for various sulfide minerals (e.g. pyrite, pentlandite, chalcopyrite). Traces elements of interest will be present from ~40

to ~1000 ppm. The RM is matrix-matched, made from the magmatic Ni-sulfide Ragland deposit. The massive sulfide was pulverized and then doped with traces elements then mixed and dried, so no water, Li, B, Ca is present in the structure. The total weight of the RM is c.a. 40g thus big enough to be shared, and analyzed by external methods. Further tests are to be completed but line scan (55 microns beam, 15 Hz, 20µm/s) show promising results to produce an innovative RM for LA-ICP-MS calibration for sulfides mineral analysis. Indeed, elements such as Se, Co, Re, Ru, Mo shows <5% RSD but improvement is needed to homogenized elements such as Sn, Bi, Zn which shows 10-15% RSD.

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PS-40**Comparison of microwave plasma atomic emission spectrometry (MP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) for the determination of scandium from Philippine laterite samples****CARMELA ALEN TUPAZ¹, CARLO ARCILLA, ROXANNE SAMOSA**¹ National Institute of Geological Sciences, Quezon (Philippines)

The Philippines is currently the largest source of nickel from laterite sources for steel manufacture. However, most of these iron-rich nickel ores are shipped directly to China because of the lack of processing facilities locally. Recent findings have indicated that Scandium, considered a precious metal because of its price, can be found in several ppm concentrations in the iron-rich laterite deposits. Data on Sc from Philippine laterite deposits are very sparse, and this is partly due to lack of analytical facilities and protocols. In this study, we compare instrumentation (MPAES and ICPMS) and sample preparation protocol approaches to Sc analyses from laterite samples, involving open acid digestion methods. Acid mixtures of HF+HNO₃ and HF+HClO₄+HCl+HNO₃ were employed both for the samples and certified reference materials. Quantitative

analysis of scandium was obtained using microwave plasma atomic emission spectrometry (MP-AES) and inductively coupled plasma spectrometry (ICP-MS), respectively. Results showed that scandium in the samples were at levels ranging from 8 – 68 ppm and obtained good precision (better than ± 10%) using the two spectrometers. Accurate determination of the element was also achieved by ICP-MS using internal standards to compensate for non-spectral interferences. Satisfactory agreement between the dissolution methods and spectrometric techniques may indicate that the analytical procedures could be suitable for quantitative determination of scandium from laterite samples. The data are important for future downstream processing of nickel and Sc-rich ores within the Philippines.

P-41**Geoanalysis at the Geological Survey of Namibia****MBINGENEKO F.¹, AMPUTU¹ M. AND GURIRAS R.¹**¹ Geochemistry and laboratory, Geological Survey of Namibia, Windhoek (Namibia)

The Geological Survey of Namibia through the Geochemistry Laboratory Division houses a wide range of modern facilities and equipment to provide analytical services to clients from the mineral exploration community, research and the general public. Laboratory services offered includes, primary and secondary sample preparation; mineral identification using the X-Ray Diffractometer (XRD); geochemical analysis using the X-Ray Fluorescence (XRF) techniques, Inductively Coupled Plasma Optical Emission Spectrometry (ICP), and the Atomic Absorption Spectrometry (AAS); and gemological studies using the polariscope and the refractometer.

Primary sample preparation for further analysis includes, the preparation of thin sections, sample drying, crushing, sieving, splitting, milling, cutting and polishing as well as heavy mineral separation. Secondary sample preparation involves acid digestion of pulverized geological material for the ICP and AAS techniques. Fusion and pressed pellets are the two standard sample preparation methods for the XRF technique. Fusion involves melting the sample with Borate flux and casting into a glass disc (platinum ware is used for this purpose). Pressed pellets are produced by pressing a mixture of sample powder with wax at 30 tons with a hydraulic press.

The identification of minerals is carried out using the XRD. The XRD lab is equipped with a Bruker AXS D8 Advance which is used for accurate identification of minerals. A wide range of minerals (including gemstones and clay minerals) can be identified using

this technique. Currently, this instrument is the only one catering for the whole country.

Geochemical analyses of geological samples are done using the, WD-XRF, ED-XRF, ICP, and AAS;

The Geochemistry laboratories are equipped with both the wavelength dispersive XRF (WD-XRF) and the energy dispersive XRF (ED-XRF) techniques. The WD-XRF is a Bruker S8 Tiger, used to analyse for a wide-range of elements at varying concentrations (major oxides to trace elements). For the ED-XRF technique, two hand-held NITON XRF are available and these are routinely used for semi-quantitative analysis of rock specimen or powdered samples. These can be used both in the laboratory and in the field.

The ICP lab is equipped with the PerkinElmer Optima 7300 DV Spectrometer, which is used for multi-element analysis at varying concentrations (major oxides to trace elements). Various sample digestion methods are applied depending on the elements of interest.

The AAS lab is equipped with the Analytik Jena ZEE nit 700, a compact spectrophotometer providing Flame AAS, Graphite Furnace AAS and Hydride AAS.

Gemological and Optical instruments available include optical polarizing microscopes and bionocular microscopes, as well as specialized gemological instruments, such as; the refractometer and the polariscope.

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Overview

	Sunday – 09/08	Monday – 10/08	Tuesday – 11/08	Wednesday – 12/08	Thursday – 13/08	Friday – 14/09
08:15						
08:30	Registration for Short Courses	Opening Ceremony				
08:40		Thomas Prohaska	Announcements	Announcements	Announcements	
09:00	Short Courses	Wilson Webb	Wolfgang Müller	Frank Melcher	Henry Longerich	
09:30	Refreshments	Begzsuren	Brand Ingham Rachetti	Malitch Cupper Dias	Garbe-Schönberg Onuk	
10:10		Refreshments	Refreshments	Refreshments	Refreshments	
10:30	Short Courses	Gäbler	Wünscher	Guillong	Refreshments	
10:50		Kirkwood Malitch	Bokhari Zack	Wiedenbeck Renno	Belousov Macholdt	
11:00		Lunch Break - included	Lunch Break - included	Lunch Break - included	Lunch Break - not included	
11:20	Lunch Break - included for SC participants					
12:00	Short Courses	Walle	Company Presentations			
12:20		Walkner				
12:40		Everett				
13:00		Havelcová				
13:20	Short Courses	Glass				
13:40		Petrakova				
14:00	Refreshments	Refreshments				
14:20	Short Courses	Molier				
14:40						
15:00		Gösser Brewery Tour, Göss				
15:20	Registration					
15:40						
16:00	Registration					
16:20						
16:40						
17:00						
18:00						
19:00						
20:00	Welcome Reception					
21:00						
22:00						
23:00						

