GEOANALYSIS
BRAZIL 2012

The 8th International Conference on the Analysis of Geological and Environmental Materials

Hotel Ferradura Resort
Buzios, Rio de janeiro, Brazil

16 – 20 September, 2012

The International
Association of
Geonalysts

Welcome!

On behalf of the Organizing Committee of The 8th International Conference on the Analysis of Geological and Environmental Materials, Geoanalysis 2012, we welcome all conference participants to Buzios, Brazil. It is our great honor to host this international meeting and we hope to fulfill the expectations of everyone. Geoanalysis 2012 has a very attractive program with an impressive number of distinguished invited speakers and lecturers. The coming days present a unique opportunity, congregating experts from various fields in geoanalysis with both students and advanced users of geoanalytical data.

What is geoanalysis? One might debate at length on this subject. Essentially its core idea is to look at the intimate nature of geological and environmental materials and to meld this knowledge with an analytical approach. The matrix and its sampling are a must to the geoanalyst. A second layer of specialized knowledge, and a subject of on-going research, is the chemical and physical principles needed to obtain the specific desired information. No less important, the data that have been produced must pass judgment: can we trust them, or better, are results and associated uncertainties satisfactory for the purposes of the study? In short, the geoanalytical field is vast and complex; this conference will present a tiny, but stimulating sampling of it.

Preparing a conference is a very demanding task. So, we wish to recognize members of the organizing committee for their individual and collective efforts to assure an excellent program. We thank our key speakers and short course lecturers for accepting our invitation to participate at this conference. We are also grateful to our sponsors and exhibitors that have provided the means to realize this conference. Finally, we wish to acknowledge Brazilian Federal and State agencies and organizations for their generous support and funding.

We wish all participants a very pleasant and fruitful week in Buzios. As one sees, the surrounding scenery is relaxing, contributing towards the spirit of congregation and sharing. We hope each and every delegate will take back with them both wonderful memories of Brazil and much increased knowledge. Enjoy!

Jacinta Enzweiler
Conference Chair

Dear Delegate,

Welcome to Geoanalysis 2012, the premier conference devote to the characterization of geochemical and environmental samples. Organized on behalf of the International Association of Geoanalysts, Búzios represents the latest venue in this triennial conference series, the ideal venue for exchanging the latest concepts in this rapidly evolving field. Whether estimating the economic viability of mineral deposits, understanding the rates of past climate change or defining the requirements for environmental remediation, the field of geoanalysis has become an essential component of many activities within our globalized society. Here in Búzios this theme takes center stage where both analysts and users of data are gathering to discuss the recent trends and to define areas where advancing methodologies can bring greatest benefit.

Initiated in Canada in 1990, this gathering in Brazil is the 8th such meeting in the Geoanalysis conference series, marking both the pinnacle and the culmination of the triennial cycle which defines IAG's activities. The five days over which we shall meet are not only an excellent opportunity to learn about the latest research advances but also provide a relaxed and informal setting to discuss one's ideas with colleagues from around the globe. Congenial settings have always been the hallmark of Geoanalysis conferences. I will take this opportunity to encourage all delegates, and in particular early career scientists, to take advantage of this unique opportunity by expanding their network of colleagues -- often the most effective means for advancing towards our common goal of a better description of our natural environment.

Búzios offers a beautiful location combined with the welcoming hospitality for which Brazil is renowned. I am certain Geoanalysis 2012 will create many happy memories for all who attend. It has been six long years since an evening in Beijing during a previous Geoanalysis when the possibility of holding this event in Brazil was first mooted. The relaxed atmosphere, excellent organization and outstanding scientific program which we will experience are the result of much toil and careful planning by this conference's organizing committee. I have closely followed the efforts which have gone into preparing Geoanalysis 2012, and I want to take this chance to thank our hosts for the excellent result of an event most well planned!

To veterans of Geoanalysis conference I'd like to say how delighted I am that we can meet again. For those new to this event might I say welcome to our community! To all delegates I say enjoy! I am confident that Búzios will provide you many stimulating ideas for advancing this fascinating field.

Michael Wiedenbeck
President, International Association of Geoanalysts

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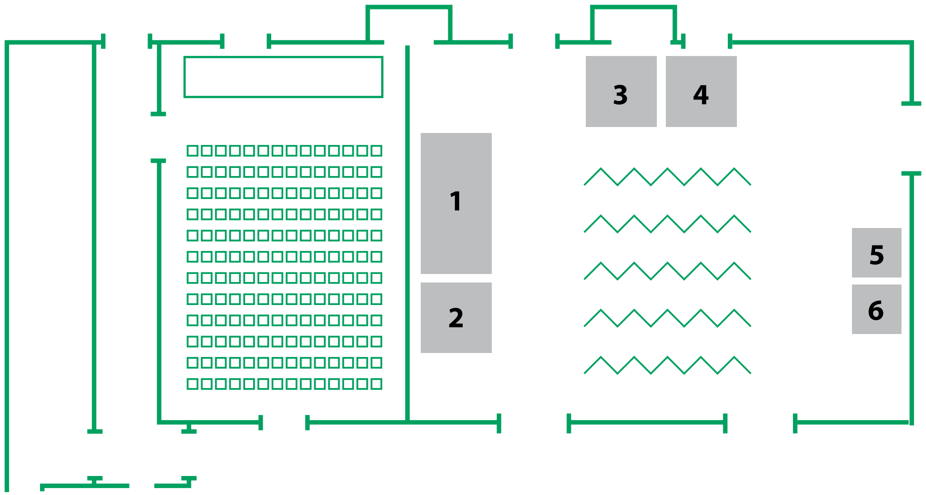
EXHIBITION



1 - analitica, Thermo SCIENTIFIC

2 - RADCHROM ANALITICA, HORIBA Scientific

3 - CAMECA SCIENCE & METROLOGY SOLUTIONS, AMETEK MATERIALS ANALYSIS DIVISION

4 - BRUKER

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6 - IAG

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LOGISTICS

SECRETARIAT

Sept 16th 18th - 8h30 - 18h
Sept 19th 8h – 12h
Sept 20th 8 – 16h

Please look for us if you have any questions.

CURRENCY

The currency in Brazil is "Real". Major credit cards (Visa, MasterCard and American Express) are accepted at most hotels, restaurants and stores. American Dollars or Euros can be exchanged at the "Banco do Brasil" in Buzios (Rua Manuel José Carvalho 70, Phone: +55 (22) 2623-2302); Banking hours are from 11 AM to 4 PM (Monday through Friday).

MEDIA DESK

Oral presentations are allocated 15 minutes (including presentation and questions).

Presentations must be prepared as MS PowerPoint files. Users of Macintosh or Linux OS must ensure their presentation is compatible with Windows OS.

When you arrive at the registration desk of the convention center, please ask to load your presentations into the allocated computer in the Business Center. Presentation files cannot be loaded at the presentation venue and personal notebooks cannot be used for presentation. We apologize for this inconvenience.

Presenters are asked to show up at the presentation venue at least 10 – 15 minutes before the session begins and report to the Session Chairperson.

The Media Desk will be open between 8 AM and 6:30 PM.

POSTERS

All posters are required to be displayed on Monday September 16th, between 8h and 10h AM and removed at the end of the Conference, on September 20th. Poster authors are required to be available for presentation during the Poster Session to meet and answer delegates' questions.

EARLY CAREER RESEARCHER AWARD

The abstracts submitted by young scientists and respective presentations/posters will evaluated by a committee of the International Association of Geoanalysts. The author of the awarded abstract will receive a certificate, 500 GBP (or equivalent in Brazilian Real) and one year free IAG Membership. Candidates for this award must meet the following criteria:

1. Doing a higher degree (PhD or doctorate) or have finished it in the past 60 months prior to the meeting.
2. To be the first author of the abstract and the work is largely his/her own.
3. To present the talk/poster personally at Geoanalysis 2012.
4. To accept the award during the closing ceremony.

CERTIFICATES

Certificates of attendance will be available at the secretariat. Poster, paper presentation, conferences, etc. will be delivered during the presentation.

BADGES

Use of badge is mandatory in all scientific and social activities. In case of lost, second route may be requested at the secretariat. Cost: $ 10

SOCIAL EVENTS

Sunday, September, 16th
19 - 21h - Welcome reception with Brazilian food and music
Ferradura Hotel – Main pool

Wednesday, September, 19th
19h – 22h
Congress Dinner at Patio Havana
Rua das Pedras, 101 – Downtown

PROGRAM

Sunday **16/09**

Time	*Activity*
8:30	Registration
9:30	***Short courses*** *Room 1* Can you trust your data? Quality assurance in analytical geochemistry **Cornelia Kriete and Thomas Meisel** *Room 2* Guidelines for better practice in LA-ICP-MS U-Th-Pb geochronology **Matt Horstwood and Jan Kosler** *Room 3* Quantitative X-ray phase analysis of geomaterials by the Rietveld method – basics, pitfalls and tricks **Reinhard Kleeberg** *Room 4* Representative sampling – the critical success - factor for geo-science analysis **Kim H. Esbensen**
10:30	***Coffer break***
11:00	***Short courses***
12:30	***Lunch***
14:00	***Short courses***
15:00	***Coffer break***
15:30 – 17h00	***Short courses***
19h00	**Welcome reception**

Monday **17/09**

Time	*Activity*
8:30	**Opening Ceremony**
	Oral Session
	Micro analytical techniques and reference materials Chairperson: Matt Horstwood
8:45	*Invited Speaker:* **Detlef Günther** Exploring New Capabilities in Laser Ablation-ICP-Mass Spectrometry
9:30	**Klaus P. Jochum** The importance of Ca carbonate and Ca phosphate microanalytical reference materials for environmental research
9:45	**Sandra Andrade** Development of correction methods for interferences by LREE oxides on the medium and heavy REE in the LA-ICPMS technique.
10:00	**Michael Wiedenbeck** Evaluating material heterogeneity at the picogram sampling scale
10:15	***Coffer break***
10:45	**Steve Wilson** Current USGS activities in the field of Microanalytical Reference Materials development
11:00	**Fabiano Faulstish** Synthesis of fluid inclusion standards
11:15	**Tobias Salge** Advanced EDX Analysis Options for Geoscience and Mining Applications using Silicon Drift Detectors (SDD) on Scanning Electron Microscopes
11:30	**Road Tagle** High speed element distribution with micro X-ray fluorescence (μ-XRF): Qualitative and quantitative analysis of major and trace elements in geological samples
11:45	**Axel Renno** Universal Presence of Elements – still a valid concept?
12:00	***Lunch***
14:30	**Technical Session**
15:15	***Oral Session:*** Isotope reference materials and applications Chairperson: **Klaus Peter Jochum** *Invited Speaker:* **Robert Vocke** "Truthiness" and Accurate Isotopic Measurements
16:00	**Debora Araújo** Investigating the use of JMC-chalcopyrite as in-house standard for in-situ Cu isotope analyses with LA-MC-ICPMS
16:15	**Miguel Basei** Lu-Hf isotopes and U-Pb ages of detrital zircons from Saldania Belt, South Africa: Stratigraphic and Tectonic Implications
16:30 – 18h30	**Poster Session** **PT01 – 32**

Tuesday **18/09**

Time	*Activity*
8:30	**Announcements**
	Oral Session
	Isotopic techniques, bulk and speciation methods Chairpersons: Michael Wiedenbeck and Gwendy Hall
8:45	*Invited Speaker:* **Thomas Bullen** Familiar faces in a strange land: the continuing search for stable isotope variability across the periodic table
9:30	**Daniel Araujo** Application of Cu and Zn isotope ratios as tracers of sources and biogeochemical process in the Paranoá Lake (Brasília, Brazil)
9:45	**Yoshikazu Kikawada** Determination of uranium isotope ratio in atmospheric deposits in Japan
10:00	**Claudia Bouman** Advances in multicollector ICPMS for precise and accurate isotope ratio measurements of uranium isotopes
10:15	***Coffer break***
10:45	**Alexandre Schneider** Sequential voltammetric determination of Zirconium and Vanadium in seawater, estuaries and rivers
11:00	**Sandra Pöhle** Determination of Zr, Hf, Nb and Ta in seawater by the use of an online-preconcentration system connected to inductively coupled mass-spectrometry (ICPMS)
11:15	**Julio Wasserman** Mercury speciation with ethylation, cryophocusing, thermal gas chromatography and detection with multi-beam atomic absorption spectrophotometry
11:30	**Anne Hélene Forstier** Use of Direct Mercury Analyzer to assess soil Hg emissions due to forest fire in the Amazonian region
11:45	**Aloísio Cotta** High temperature acid dissolution of silicate rock samples
12:00	***Lunch interval***
15:00	***Oral Session:*** Isotopic methods applied to atmospheric studies Chairperson: **Marly Babinski** *Invited Speaker:* **Dominik Weiss** Proxies of atmospheric transport, their connection to biogeochemical cycles and paleoclimate studies
15:45	**Simone Gioia** Zn-Pb-Sr Isotopes as pollutant tracers in aerosol samples of São Paulo city - Brazil
16:00	**Coffee**
16:30	**Poster Session** **PT33 – 63**
17h45	**IAG General Meeting**

Wednesday **19/09**

Time	*Activity*	
8:30	**Announcements**	
	Oral Session	
	Session in honor of Phil Potts Chairperson: Thomas Meisel	
8:45	*Invited Speaker:* **Gwendy Hall** Evaluation of the performance of portable XRF in the mineral exploration and mining industry	
9:30	**Michael Ramsey** Evaluation of *in situ* heterogeneity of elements in solids: implication for geoanalysis	
9:45	**Nick Walsh** Precision, Accuracy and Some Uncertainty in Silicate Analysis	
10:00	**Thomas Meisel** Modifications of the IAG Certification Protocol according to recent developments in metrology	
10:15	***Coffer break***	
10:45	**Phil Potts** 40 years in geoanalysis – a personal perspective	
11:30	**Doug Miles** An unselfish meme - the Early Days of the IAG	
11:45	**Messages and conclusion**	
12:00	***Lunch***	
12:15	**Free**	**Renata Schmitt** Buzios Geology
13:30		**Búzios Field Trip**
19:00	**Conference diner**	

Thursday **20/09**

Time	*Activity*
8:30	**Announcements**
	Oral Session
	Sampling, quality assurance and reference materials Chairpersons: Phil Potts and Maggi Loubser
8:45	*Invited Speaker:* **Virginia Ciminelli** Geoanalytical needs to conciliate mineral production with water resources, biodiversity and cultural heritage conservation
9:30	**Kim Esbensen** Counteracting Heterogeneity in Sampling and Analysis – Theory of Sampling (TOS) vs. Measurement Uncertainty (MU)
9:45	**Richard Conrey** WDXRF Analysis of Small Samples; How Low Can We Go?
10:00	**Maggi Loubser** The preparation and certification of in-house reference materials for XRF calibration.
10:15	***Coffer break***
10:45	**Phil Potts** An assessment of analytical performance in the routine analysis of silicate rocks: An analysis of data submitted by geochemistry laboratories participating in the GeoPT proficiency testing programme – 2001 to 2012
11:00	**Brian Marshal** Quality Assurance in the U.S. Geological Survey Energy Geochemistry Laboratory
11:15	**Cornelia Kriete** Quality Assurance in the European Geochemical Mapping Project GEMAS
11:30	**Stephen Wilson** USGS/EPA development of bioavailability reference material SoFC-1 used in the toxicological evaluation of arsenic and lead
11:45	**Dai Hong Luo** The preparation of three polluted soils and ore mine waste as reference materials
12:00	***Lunch interval***
14:00	***Oral Presentation*** Chairperson: **Rômulo S. Angelica** *Invited Speaker:* **Paulo Vasconcelos** The environmental crystallography of goethite, or is there such a thing as a crystallographic standard?
14:45	**Poster session** **PT 64 -90**
16:00	**Closing Ceremony**

ABSTRACTS

INVITED SPEAKERS

Exploring New Capabilities in Laser Ablation-ICP-Mass Spectrometry

DETLEF GÜNTHER,
ETH Zürich, Department of Chemistry and Applied Biosciences, Wolfgang Pauli Strasse 10, CH-8093 Zürich, Switzerland

Laser ablation-inductively coupled plasma mass spectrometry has been successfully applied to a wide variety of solid samples for major, minor, trace element analysis or isotope ratio determinations. Beside remaining limitations it has been shown that the precision and accuracy in direct solid analyses improved continuously over the last decade. This has mainly to do with progress in laser technology and the fact that sampling, aerosol transport and excitation processes have been studied in great detail, leading to improved quantification strategies.

The most recent trend in LA-ICP-MS is focused on quantitative, high spatial resolution elemental mapping, which is required to reconstruct the trace element distribution in tissues, in stalagmites or in alloys and steel samples, meteorites and many others. Therefore, low dispersion and sample-geometry independent ablation cells have been developed, which allow monitoring minimum changes in trace element concentrations. Some most recent ablation cell geometries will be discussed and their features on selected applications will be shown. A recently introduced atmospheric sampling system, currently in the third generation, allowing the analysis of samples without an airtight ablation cell will be explained and some promising applications will be discussed in detail [1].

In addition, strategies for selective removal of elements from laser-generated aerosols by electrothermal vaporization prior to the analysis by ICP-MS will be discussed and examples for isotope ratio measurements will given [2].

Besides a lot of improvements, the lack of reference materials requires the use of non-matrix matched calibration materials for quantification. However, this quantification approach is not generally applicable and the results differ in accuracy. Therefore, laser-generated aerosols and single particles were introduced into the ICP and studied by using optical emission spectroscopy, particle imaging velocimetry and laser light scattering. These studies will demonstrate that the onset of particle vaporization is one of the most crucial parameters for accurate and precise quantification in LA-ICP-MS.

Furthermore, various strategies for producing well defined and matrix matched calibration materials were investigated. Especially the production of precious metals containing samples was tested. Preliminary results, including homogeneity studies on the newly synthesized materials will be discussed.

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[1] Kovacs, R., Nishiguchi, K., Utani, K., Günther, D., Development of Direct Atmospheric Sampling for Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry. J. Anal. At. Spectrom., 2010, 24, 142-147

[2] Brogioli, R., Hattendorf, B., Koch, J., Wiltsche, H., Flamigni, L., Günther, D. Online electrothermal heating of laser-generated aerosols: effects on aerosol particle size and signal intensities in ICPMS. Anal Bioanal Chem, 2011, 399 (6), 2201-2209

“Truthiness” and Accurate Isotopic Measurements

ROBERT D. VOCKE, JR.
National Institute of Standards and Technology,
Gaithersburg, Maryland, USA (vocke@nist.gov)

The New Oxford American Dictionary defines truthiness as “the quality of seeming or being felt to be true, even if not necessarily true” and this definition can readily be applied to the current state of accurate or absolute isotopic measurements. How can this be? And perhaps more importantly, how do we get our measurements back to the desired state of rigorous “truth” as opposed to its pale cousin, “truthiness”?

The traditional approach to ensuring accuracy in isotopic measurements invariably involved the use of isotopic Reference Material (iRMs). However, the measurement precision currently achievable by modern multi-collector mass spectrometers has taken us well past the accuracy of our traditional iRMs. Furthermore, with the maturation of powerful ionization sources attached to these mass spectrometers, the entire periodic table has become a fertile hunting ground for small but significant natural isotopic variations produced by new and novel processes. This is where the dilemma associated with “truthiness” starts to arise. Often, out of sheer necessity, the production and value assignment of new iRMs for these innovative applications are done by the pioneering researchers themselves. Most value assignments are then based on “best measurements” by the original groups. Research groups generally have a “favorite” model to correct for mass discrimination and other influences affecting a materials’ isotopic signature. The models frequently differ depending on the group, a situation that leads to a proliferation of diverse values which depend more on a research group’s philosophy than on the rigor of their measurements. This is a highly confusing and potentially non-constructive situation that leads naturally to truthiness!

Fortunately, iRMs remain the most important tool for resolving these problems. This talk will address how such reference materials can lead us out of this muddle when chosen, characterized and used wisely. The root premise here is that any homogeneous iRM measured anywhere in the world should give the same isotopic abundance ratios within analytical uncertainty. This is the goal! I will discuss approaches to choosing and characterizing new and existing iRMs and examine the current state of the practice. The goal has remained quite elusive, but perhaps with the right tools, we can now realize the promise of accuracy and high precision.

Familiar faces in a strange land: the continuing search for stable isotope variability across the periodic table

THOMAS D. BULLEN,
U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025 USA
tdbullen@usgs.gov

Incredible leaps in our ability to determine the stable isotope composition of metals and metalloids over the past two decades have fueled an expanding interest in exploring isotopic variability across the periodic table. While the steadily increasing numbers of multi-collector inductively coupled plasma mass spectrometers in research institutions and universities has been central to the advance of this field, thermal ionization mass spectrometers have likewise found their niche as the analytical platform of choice for certain elements. Gradually, an increasing number of igneous and metamorphic geochemists familiar with these instruments are turning their talents for analysis of radiogenic isotope systems toward the investigation of metal and metalloid stable isotope systems, often finding unexpected results. Although we were confident early on that light elements such as lithium and boron were likely to have large ranges of stable isotope composition in natural materials, it came as an unexpected yet pleasant surprise when significant mass dependent and mass independent variability of mercury stable isotope compositions were demonstrated for natural materials. Recent recognition of natural stable isotope variability for other heavy elements such as strontium, barium and uranium have led to the perception that almost anything is possible in this field, and geologists, hydrologists, biologists and biomedical specialists are incorporating these new tools into their research. However, euphoria aside, it is now likewise clear that many of the same issues that confronted the gas stable isotope field decades ago are finding their way into metal and metalloid stable isotope science. Debates over the relative importance of kinetic vs. equilibrium reactions and biologic vs. inorganic controls, and even the robustness of analytical approaches now dominate the discussions at conferences and in the literature. On the analytical front for example, while some isotope systems can boast rigorously characterized standards, there are as yet no accepted standards for many of the studied isotope systems. Moreover, a variety of measurement techniques including standard-sample bracketing, internal standardization, and double spiking are used, but efforts to validate the data are rare. Confronting these and other analytical issues pose a major challenge for the continued advance of this adolescent field.

Proxies of atmospheric transport, their connection to biogeochemical cycles and paleoclimate studies

DOMINIK WEISS
Imperial College London - UK

Atmospheric trace element and mineral dust cycles make our Earth System work. They control the fertilisation of nutrient deprived ecosystems, change the radiation balance of the atmosphere and affect its heterogeneous chemistry. A thorough quantitative and qualitative understanding of sources and deposition is therefore key to the successful development of regional climate and pollution models.

The extent and timing of external forcing (natural or man made), however, can only be understood and quantified if their temporal and spatial evolution is documented by using environmental records and by monitoring atmospheric particulate matter.

In this lecture I will review recent advances in our understanding of past and present atmospheric dust and trace element cycles and discuss the analytical challenges associated with it. My focus will be on: (i) the development of peat and lichens as records of past and present atmospheric mineral and trace element fluxes; (ii) the application of non radiogenic and radiogenic stable metal isotope systems and rare earth elements to identify dust and pollution sources; (iii) the past atmospheric dynamics of the Asian monsoon system and (iv) the importance of growing economies on global biogeochemical trace element cycles.

Evaluation of the performance of portable XRF in the mineral exploration and mining industry

GWENDY E.M. HALL
Geological Survey of Canada, Ottawa;
ghall@nrcan.gc.ca

This presentation describes the results of a study of the performance of five portable ED-XRF (pXRF) instruments in the analysis of a suite of 40 geological control reference materials ranging from igneous and sedimentary rocks of 'background' element concentrations through lake and stream sediments to sulphide ores. In addition to accuracy and precision, the other parameters studied include beam time, drift and thin-film type and thickness. The project was funded by CAMIRO (the Canadian Mining Industry Research Organisation), with more than 30 industry sponsors and Natural Resources Canada; the three handheld and two benchtop instruments were on loan to the project by Olympus (InnovX), Thermo Fisher Scientific (Niton) and Bruker Elemental. The second phase of this project focussed on more practical problems in portable XRF application, such as the effects of: wetness of the sample, grain size distribution, surface conditions and texture of the sample, and different chemical matrices.

Perhaps the most surprising discovery is the inconsistency in performance from one instrument to another, beyond that to be expected when using five instruments with three different target anodes (Rh, Ta and Ag). Large differences in accuracy are evident for many elements, mostly the traces. The order of best to worst performance depends on the element and the matrix; such variation in results across the instruments makes conclusions challenging. Since the hardware used by these manufacturers is similar, the differences in the figures of merit obtained probably arise from the particular algorithms employed by the manufacturers.

Time restrictions precluded calibration in the mining mode (Fundamental Parameter approach) specific to each of the wide-ranging matrices under study and thus given that factory calibration alone was used, one would expect more accurate results when calibrating with like-matrices. It is interesting that particular groups of samples, such as mafic/ultramafic rocks, felsic rocks or soils, did not show distinctly different calibration behaviour in the plots of 'pXRF value' versus 'recommended value'. Using the summary of r2 (goodness of fit to the line) and slope, the overall sequence of elements in the mining mode from 'good' to 'bad' in this mode is Fe, Ca, Zn, Pb, Cu, Si, K, Al, S, Cr, As, Ni, Mn, Ti, Sr, Rb, P, and Mg.

In the soil mode (using Compton Normalisation), the sequence from best to worst element is Sr, Rb, Cu, Ca, K, Zn, Fe, Ti, Zr, As, Mn, Th, Pb, Nb, Ba, Cd, Cr, U and Sb. For these elements, a minimum of one 'good' rating for accuracy (slope of 0.96-1.04) or goodness of fit (r2 >0.9) was assigned to at least one instrument. However, elements where all ratings are 'fair' (slope of 0.9-0.95 or 1.05-1.1; r2 of 0.8-0.9) 'poor' or 'bad' (slope of <0.8 or >1.2; r2 <0.5) include Mo, V, Ni, Co, S and Sn.

Elements where highly erroneous results were obtained include Au, Bi, Cs, Hf, Hg, Sc, Pd, Pt, Se, Ta, Te and W. While many values for these trace elements are below detection limits set by the factory, others are reported in some samples at ~10- to 1000-times higher levels than the accepted concentrations. Clearly these elements suffer from acute spectral interferences, made far more prominent by the element's normal abundance in the ppb rather than ppm concentration range. Some of the most severe interferences were those evident in the analysis of rare earth element-enriched samples where the first row transition elements were severely compromised.

Repeatability of measurement by pXRF is usually excellent, often better than ± 10 %, depending on concentration and region of the spectrum being measured. Typical RSDs for the CRMs are in the ranges: <2.5 % for Fe, Ca, K, and Si; 2.5-4.9 % for Mn, Rb, Sr, Ti, Y, Zn, Zr; 5-10 % for Ag, Cr, Cu, Pb, V, Al, S; and 11-20 % for As, Ba, Cd, Co, Ni, S, Th, U, Mg.

Although the benchtop instruments are operated at higher power than the handhelds, and therefore should be superior for elements whose lines are of higher energy, there was no perceptible difference in performance.

It is clear from this study of these 40 CRMs that further improvement in software is needed to mitigate the interferences encountered in the analysis of geological samples, which are far more varied in their composition than, for example, alloys where analysis by pXRF is well established. Indeed, this project has led to changes in the manufacturers' approach to calibration. Examples of the results of the second phase of this project will also be included in this presentation.

Portable XRF is a very useful rapid analytical tool for guiding surveys, classifying lithology, and sorting samples and drill-core. It is by no means a replacement for the high quality data generated by an accredited geochemistry laboratory. It must be borne in mind that the actual amount of sample being analysed is very small, with a depth of analysis ranging from µm (light elements) to mm (heavy elements) and therefore comparison of results to a bulk analysis where, for example, a large, perhaps heterogeneous, rock sample has been crushed, ground, milled and analysed in a laboratory is not valid. Oftentimes in a field application it is the spatial trend in concentration that matters, not the accuracy. The feature of pXRF that limits its performance in bulk geoanalysis – its small window of measurement of 1 cm diameter or less - should be utilised more in exploration to provide valuable spatial information.

Distinguish Lecture
40 Years In Geoanalysis – A Personal Perspective

PHILIP J. POTTS
Emeritus Professor of Geoanalysis, Faculty of Science, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK (Phil.j.potts@gmail.com)

Forty years ago, wavelength dispersive XRF and neutron activation analysis were front line research techniques, a number of laboratories continued to support arc source atomic emission for routine trace analysis, the inductively coupled plasma had not been commercialised as a viable technique for either atomic emission or mass spectrometric analysis, lasers had not been miniaturised to the point where they could be incorporated into an analytical technique, the first computed automated electron microprobe was just being designed but with significantly less computer power than is available in a smart phone, there was a relatively informal way of characterising new geochemical reference materials, and geochemical research was dominated by understanding processes associated with plate tectonics with the expectation of new horizons being revealed in planetary science as a result of the US Apollo missions to the moon.

When compared with today, there have been a substantial number of drivers for change. In terms of instrumentation, the development of first, the integrated circuit, and then the microchip, with the consequent miniaturisation of instrumentation has had a huge impact of both costs and operability. The taming of both the analytical laser and the analytical plasma has created new categories of instrumentation. The expectation that trace and isotope ratio measurements traditionally undertaken on bulk samples should be achievable in individual minerals with new forms of microprobe instrumentation has largely been delivered. International developments in quality systems has imposed regulation on the operation of many analytical laboratories, not the least being the need for accreditation, proficiency testing and the criteria for the development of certified reference materials. And the priorities for geochemical research have changed as well, with climate change, as illuminated by changes in the geological record, achieving as much prominence and funding as conventional geochemical studies.

The aim of this presentation is to review these trends from the personal perspective of career in geoanalysis and to make some predictions for future developments in this field.

Geoanalytical needs to conciliate mineral production with water resources, biodiversity and cultural heritage conservation

VIRGINIA S.T. CIMINELLI [1,2]
1 Instituto Nacional de Ciência e Tecnologia em Recursos Minerais, Água e Biodiversidade.
2 Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal de Minas Gerais-UFMG, Av. Antonio Carlos, 6627, Escola de Engenharia, Bloco 2, s/3422, Campus Pampulha - 31270-901, Belo Horizonte - Minas Gerais - Brazil – ciminelli@demet.ufmg.br

The feasibility and competitiveness of mining operations are increasingly dependent on social approval. Communities are mobilized to better understand how industrial activities will affect the social, economic and environmental future of their hometowns, and to influence law making and enforcement. The industry is driven to positively respond to stakeholders concerns, demonstrating with comprehensive approaches and long-term vision, the role of the enterprise to promote economic and social development of the target territories. Regions where the mineral commodities play a major economic role are then urged to develop appropriate information and mediation systems.

Perhaps none of the stakeholders, even the more skilled ones, are prepared to deal with issues raised by the complex, multiple boundaries of mining operations with watersheds, nearby urban, protected and culturally valued areas, that make the environmental management increasingly difficult. A question that can be asked is: How can one accurately measure the impact of a mining operation beyond the industry's boundaries, considering its multiple interfaces and sources of contamination?

A second key question is related to the potential, long-lasting risks associated with the disposal of tailings and waste rock, and to the final pit lake. How can one rigorously determine the conditions that will ensure the structural and chemical stability of the wastes and tailings materials now and in the foreseeable future? Development of precise indicators to evaluate the eventual impacts on surface and groundwater quality and quantity, air and soil quality, biodiversity richness are needed.

These challenges create unique opportunities for scientific and technological development, and capacity building. Geoanalyses are strongly required to assess the environmental impacts and to guide innovative approaches for the recovery of impacted areas. Industrial processes should be redesigned for a better environmental performance, and finally, relevant information should be made accessible to all stakeholders. The need for solutions that take into account the specificities of each site empower local communities as well as the local chain of technology and knowledge suppliers. Examples of the INCT-Acqua's experience with the aforementioned issues are provided. Emphasis is given on the geolanalyses needed to help in establishing a model for industrial development reconciled with the preservation of water resources, biodiversity and cultural heritage.

The Environmental Crystallography of Goethite, or is There Such a Thing as a Crystallographic Standard?

ALBERT MOSTERT, PAULO VASCONCELOS, AARON SEEBER AND KURT KNESEL
School of Earth Sciences, University of Queensland, The University of Queensland
School of Earth Sciences, Steele Building, Brisbane - Qld 4072, Australia
paulo@earth.uq.edu.au

Abstract

Rietveld refinement of synchrotron powder X-ray diffraction data for synthetic goethite precipitated at distinct pHs (<2 and >10) and various temperatures (22, 40, and 70 °C) reveals a strong correlation between crystallographic parameters (e.g., crystallite sizes and unit-cell dimensions) and environmental conditions during mineral precipitation. Temperature and pH also control crystallite sizes and unit-cell dimensions in Al- and Ni-goethites. Importantly, environmental conditions strongly control the uptake of metal dopants during mineral precipitation. The synchrotron X-ray diffraction data conclusively reveal that variations in powder diffraction data for goethite depend on ambient conditions prevailing during mineral precipitation. The results also suggest that, with proper calibration, variations in high-resolution diffraction patterns for minerals may be a powerful environmental indicator – environmental crystallography – that complements ambient information retrievable from mineral habit, texture, composition and isotopic signatures. Since powder diffraction data for a mineral varies with polytypes, chemical varieties, differences in hydration, order-disorder, etc., environmental crystallography may become an effective tool for determining factors that control these structural variations.

ABSTRACTS

ORAL PRESENTATIONS

OP.01

The importance of Ca carbonate and Ca phosphate microanalytical reference materials for environmental research

K.P. JOCHUM[1], S. WILSON[2], B. STOLL[1], U. WEIS[1] AND M.O. ANDREAE[1]
1 Max-Planck-Institut für Chemie, Postfach 3060, 55020 Mainz, Germany
2 U.S. Geological Survey, Box 25046, Denver Federal Center, Denver CO 80225, USA

The high spatial resolution available with LA-ICP-MS microanalysis of speleothems, biogenic calcium carbonates, bones and teeth holds the promise to improve the understanding of past climate conditions and environmental change. However, there are some analytical problems with this method, such as interferences, elemental fractionation and mass-load-dependent matrix effects, when using non-matrix-matched reference materials. We have therefore investigated the silicate NIST and geological MPI-DING glasses, as well as the new Ca carbonate MACS-1 and MACS-3, and the Ca phosphate MAPS-4 and MAPS-5 microanalytical reference materials (RM) from the USGS.

Our studies with a sector-field ICP-MS and two Nd:YAG lasers with 213 nm and 193 nm wavelengths, respectively, show that many masses are affected by interferences, such as $^{24}Mg^+$ by $^{48}Ca^{++}$, $^{31}P^+$ by $^{15}N^{16}O^+$ in the carbonate, and $^{47}Ti^+$ by $^{31}P^{16}O^+$ in the phosphate matrix. Elemental fractionation and mass-load-dependent matrix effects have been detected for both laser systems. They are small for refractory lithophile elements, especially when using the 193 nm laser (< 5%). For chalcophile/siderophile trace elements with low boiling points (e.g., Pb, Zn), however, these effects are high (up to 40% and 15% for 213 nm and 193 nm lasers, respectively) and different for the NIST silicate glasses, the geological MPI-DING glasses, and the carbonate and phosphate RM.

This means that the commonly used NIST glasses are suitable as calibration material for carbonate and phosphate LA-ICP-MS microanalysis of lithophile refractory elements, but that matrix-matched calibration is still preferred for an accurate analysis of chalcophile/siderophile elements, especially when using a 213 nm laser.

We have determined the concentrations of lithophile trace elements in MACS-1, MACS-3, MAPS-4, and MAPS-5 using LA-ICP-MS with NIST 610 and 612 for calibration. Overall analytical uncertainties at the 95 % confidence level are about 5 – 10% for most elements. Our results agree well with available preliminary reference values and concentration ranges.

In order to analyze precisely and accurately carbonate and phosphate samples for environmental research by microanalytical techniques, the production and certification of carbonate and phosphate microanalytical RM is an urgent task for RM producers.

OP.02

Development of correction methods for interferences by LREE oxides on the medium and heavy REE in the LA-ICPMS technique

SANDRA ANDRADE(1), HORSTPETER H.G.J. ULBRICH(1), VALDECIR A. JANASI(1), LUCELENE MARTINS(1)
(1)Instituto de Geociências – USP – Rua do Lago, 562 – Cep.: 05508-080- São Paulo, SP, Brasil, email: sandrade@usp.br

Laser Ablation coupled to ICP-MS is a powerful tool for in-situ analysis of geological materials. The interferences caused by generation of isobaric molecular species inside the plasma or at the extraction interface are an important limitation. The main interferences are the MO^+ and MOH^+ species; examples are the barium oxide effect on LREE (Eu) and LREE (La, Ce) on the medium and heavy REE (Gd, Tb, Er, Tm).

Generation of REE oxides during analysis of rock solutions by ICP-MS technique, as well as the correction methodology for these isobaric interferences has already been widely discussed in the literature (Aries et al. 2000, *Geostand. Newsl., 24: 19-31)*. However, a simple method for corrections does not exist for LA-ICPMS procedure, despite proposals by Kosler et al. 2002 (*Anal. Bioanal. Chem, 374: 251-254)* and Kent et al.,2005 *(J. Anal. At. Spectrom., 20: 1256-1262)* that have shown the significant contribution of these molecular species in materials where the Ba/Eu > 1000 or $[La/Gd]_N > 3$. These relationships are found in materials such as reference rock glasses (e.g. BCR-2G, T1G), alkali feldspars with high Ba concentrations and minerals rich in LREE, as apatite, monazite, etc.

A methodology is here proposed for the determination of molecular species MO^+ and MOH^+ oxides and hydroxides of LREE, especially in apatite, and the interference corrections in LA-ICPMS methods for medium and heavy REE. This study used synthetic materials, similar to monazite and/or xenotime, obtained by fusion of common REE phosphates at temperatures of 1100 to 1300°C in the presence of fluxes containing mixtures of MoO_3, Li_2CO_3 and Na_2CO_3 (Cherniak et al. 2004, *Amer. Mineral., 89: 1533-1539).* Chemical and mineralogical characterization of these materials must precede their use as standards of molecular interference corrections.

Key words: LA-ICMS, molecular interferences, REE, phosphates, apatite.

OP.03

Evaluating material heterogeneity at the picogram sampling scale

WIEDENBECK M - Helmholtz Centre Potsdam -
Inorganic and Isotope Geochemistry

An increasing spectrum of laboratory methods is capable of quantifying elemental and isotopic compositions of geomaterials at well below the nanogram sampling scale. As an example, for several decades electron probe microanalysis (EPMA) has provided major element determinations on sample volumes of only a few µm3, equivalent to a few picograms of total sample mass. This method is rather insensitive to the nature of the matrix being analyzed; hence, pure substances or stoichiometric compounds can be used for calibration and validation purposes once appropriate corrections have been applied.

Other methods, and in particular secondary ion mass spectrometry (SIMS), are more strongly influenced by the composition of the material being analyzed, resulting in a critical need for matrix matched reference materials. Here the analyst comes up against the barrier that there are currently no substances certified for use as geochemical reference materials at sub-nanogram test portion masses. SIMS is a highly sensitive method, meaning that it is often the only analytical technique capable of assessing trace element or isotopic compositions at the picogram mass range. This generates the conundrum that SIMS is needed to characterize the heterogeneity of reference samples ultimately intended for SIMS calibration, where the analytical uncertainties from the homogeneity testing must be propagated into the uncertainty budget for the values assigned to the reference material.

This presentation will explore a number of strategies which can be used to reduce the uncertainty contribution from the heterogeneity component. One option is to compare the distribution of results to those obtained from a similar, assumed to be homogeneous material. An alternative approach is based on the assumption that sample heterogeneity decreases as a function of length scale: i.e., measuring points which are closely clustered should reveal less heterogeneity than sampling which is conducted over a larger area. Mathematical methods – which are yet to be fully developed – would thus allow the variance observed at small spatial scales (10’s of microns) to be used to estimate the heterogeneity over larger spatial scales (millimetres or between sample fragments). Such refined heterogeneity estimates could then be applied to quantitative results obtained from bulk samples.

OP.04

Current USGS activities in the field of Microanalytical Reference Materials development

S.A. WILSON, A. KOENIG, R. A. ORKILD-NORTON
U.S. Geological Survey - Geologic Division

Discussions will focus primarily on the physical and chemical characterization of several new MRMs used in the analysis of black coral and both modern and fossilized bone material. Black coral because of it high organic content and unique trace metal composition required a new approach in terms of creating a calibration material with the proper homogeneity. We combined an epoxy based matrix with a customized blend of 22 trace metals contained in a high organic medium. The addition of Re and U, two critical elements found in black coral was accomplished using an acetone based solvent extraction process. The acetone phase combined with the trace metal material was mixed with the epoxy components and allowed to harden for a period of 24 hours. The material identified as MAOS-X was prepared in a series of discs containing 24 elements at concentrations ranging from 20 – 200 ppm. LA-ICPMS analysis (193 nm laser, 50 micron spot size) of random discs revealed elemental precisions of between 3% and 9% for all 24 elements. Discussion will focus on the use of this material in the analysis of black coral samples and potential use for other organic based sample types

In support of laboratories activities dealing with the analysis of bone samples, two materials were prepared using a USGS developed co-precipitation process. The materials identified as MAPS-4 and MAPS-5 are representative of fossilized and modern bone material respectively. The apatite based matrix was doped with 50 minor and trace elements at concentrations ranging between 5-200 ppm (MAPS-5) and 500-2000 ppm (MAPS-4). Using bulk analysis from a select set of international laboratories preliminary recommended element concentrations were determined. LA-ICPMS analysis shows precision values of less than 10% for all trace and minor elements. Discussion will focus on the evaluation of element homogeneity, and use of these materials during the analysis of various bone samples.

OP.05

Synthesis of fluid inclusion standards

FAULSTICH FRL[1], NEUMANN R[1], PIRONON J[2], RANDI A[2]
[1]CETEM - SCT/COAM, [2]Université de Lorraine - Géologie et Gestion des Ressources Minérales et Energétiques

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Fluid inclusions are samples of fluids trapped in microcavities of minerals, keeping the pressure, temperature and fluid composition of the system when the crystallization, recrystallization or healing of microfractures of the host mineral took place. The study of fluid inclusions is the only way to assess this fluid composition, an otherwise scarce and valued information for the reconstruction of the geologic evolution.

The method of choice for the quantitative analysis of fluid inclusion composition is Raman spectroscopy, due to micrometric inclusion size, hosted inside the mineral, and fluid composition. The spectroscopic approach requires calibration curves, meaning a range of inclusions of similar composition in similar matrixes. These fluid inclusion standards must be synthesized.

Here we detail the procedures to synthesize inclusions of fluids of known composition under diagenetic conditions: low temperatures (50 - 180°C) and pressures (20 - 250 bar) included in quartz. We use pre-existing microcavities in quartz polished chips, decrepitated and rinsed before healed in an autoclave. Each synthesis requires around four weeks.

Diphasic liquid-vapour inclusions in the H2O-CH4-NaCl system were synthesised, varying the content of all three components. The quartz chips were checked before and after synthesis by optical microscopy (decrepitation of former inclusions, neoformation of diphasic inclusions) and Raman spectroscopy (composition of former and synthesis fluids), and the methane-water molar fraction was determined by Raman microspectroscopy. Salinity was determined by microthermometry.

The main advantages of the chosen procedure against other published methods are: quicker healing of the microfractures formed by decrepitation of former inclusions, and at lower temperatures; larger inclusions, chosen among the samples prior to decrepitation, allowing better quantification; simple quartz sample preparation and use of commercial, from-the-shelf, reactors, precluding precious metal capsules and not requiring any specialized tool or equipment.

The method was used to build a series of calibration curves relating methane-to-water count ratios to the methane content of aqueous fluid inclusions, covering salinities from 0 to 15% NaCl (eq), and the aforementioned pressure and temperature ranges. Good correlation curves have been obtained between Raman band area ratios and expected CH4 solubilities from Duan's model (2006).

OP.06

Advanced EDX Analysis Options for Geoscience and Mining Applications using Silicon Drift Detectors (SDD) on Scanning Electron Microscopes

T. SALGE AND J. BERLIN
Bruker Nano GmbH, Schwarzschildstr. 12, 12489 Berlin, Germany. tobias.salge@bruker-nano.de.

Recent developments in SDD technology combined with improved atomic databases and modern data processing offer advanced analysis options for element analysis. This paper presents challenging applications using the QUANTAX EDS system. The main advantages of SDDs are their high pulse throughput capabilities (up to 600 kcps) and an improved energy resolution (down to 121 eV for Mn-Kα) – even in the low energy range (38 eV at C-K). To separate overlapping peaks by deconvolution, Bruker Nano's atomic database incorporates more than 300 additional L, M and N lines in the low energy range of 0-6 kV [1]. Data processing with modern computers sets the stage for spectrum imaging (an entire EDX spectrum is collected at each pixel during a mapping), offering advanced data mining. Stage control allows large data sets to be acquired within a short time. Feature analysis is an automated particle search with chemical classification. For maximum accuracy, standardless and standard-based analysis can be combined into a hybrid quantification.

Application examples include (A) Drill core analysis by large-area and high-resolution mapping. Two samples will be discussed from the Chicxulub impact crater (K/Pg boundary): the ejecta sequence at OPD leg 207 containing shocked carbonates [2] and an impact melt breccia of the Yax-1 borehole revealing resorbed garnets [3]. (B) Modal analysis with chemical phase mapping on a sulfate-carbonate-dominated matrix sample of borehole UNAM-7 from the Chicxulub crater [4]. (D) Classification of minerals in complex systems by feature analysis: Calcite can be discriminated from fluorite with an improved light element quantification. Hybrid quantification allows classifying magnetite, hematite, silicates and phosphates. Deconvolution of REE allows classifying different generations of monazite.

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OP.07

High speed element distribution with micro X-ray fluorescence (µ-XRF): Qualitative and quantitative analysis of major and trace elements in geological samples

R. TAGLE, M. HASCHKE AND T. SALGE
Bruker Nano GmbH, Schwarzschildstr. 12, 12489 Berlin, Germany. Roald.Tagle@bruker-nano.de.

X-ray fluorescence is an analytical method well known in the field of geochemistry. The micro X-ray fluorescence (µ-XRF) adds to the potentials of the XRF the spatial resolution by using a polycapillary X-ray optics allowing study compositional variation within samples. Thereby, the distribution of elements can be analyzed non-destructive at high sensitivity.

Significant technological improvements in µ-XRF are a result of advances in the silicon drift detector technology (SDD), which significantly decreases measurement time. Enhancement of the polycapillary X-ray optics allows to display the distribution of elements with Z>10 starting from sodium and trace elements (down to 20 ppm) with a spatial resolution down to 25 µm. These together with the strong capabilities of signal and data processing technologies (data mining) has allow for the first time to develop an instrument with a lot of potentials in the study of geological samples.

Some of the potentials of µ-XRF for the qualitative and quantitative element analysis of geological samples can be summarized as follows: (1) Large samples in the decimeter scale can be analyzed without complex sample preparation. The µ-XRF allows determining the element distribution of large geological samples, e.g. mineral assemblages, or even to document the composition of a large number of thin sections for later detail study with the electron microscope. As vacuum is only required to improve detection limit of light elements, it is possible to work at air, therefore not only solid but also wet or liquid samples can be analyzed e.g. drill core sections of wet sediments or oil rich rocks. (2) Quantification using fundamental parameter allows determining the trace element composition in a sample with high precision, e.g. trace element composition of minerals and volcanic glasses.

OP.08

Universal Presence of Elements – still a valid concept?

RENNO AD
Helmholtz Institute Freiberg for Resource Technology

In 1936 Ida Noddack published her landmark paper "Über die Allgegenwart der chemischen Elemente" (Noddack, 1936). In this article she states: „All chemical elements are present in all minerals." This conclusion was based in the painstaking trace element analysis of bulk minerals. She was able to document the presence of such chemical elements as Re in sphalerite down to 10 ng/g (Noddack, 1936).

It was, of course impossible for her to anticipate the development of modern microanalytical instrumentation, which is able to operate routinely at the picogram test portion range.

The Helmholtz-Institute Freiberg for Resource Technology is currently working to establish the Super-SIMS method (Döbeli et al, 1994) for analysis of minerals, and ores. The extreme sensitivity of this technique raises the question of the validity of the concept of Universal Presence of Elements. It is expected that the Super-SIMS we will be able to quantify some elements down to the 1 ng/g level (10-12 atoms/atoms) in ideal matrices. Using a commercial available ion probe we will be able to focus the ion beam down to 2 µm in diameter, equivalent to a sampling mass at or below the sub-ng level.

Simulations of the probabilities of finding elements of interest at such low target concentrations show that the Super-SIMS will reach the point that the chance of measuring these elements in such small sampling volumes will be less than 10 %.This leads to a number of new questions which need to be addressed when addressing the topic of a given element yes-or-no. Is it still possible to describe the geochemical behavior of ultratrace elements if the probability of detection of such elements in very tiny volumes approaches zero? What are the driving forces behind the geochemical behavior of such ultratrace elements? We hope that the new Super-SIMS facility will help to answer such question in the not too distant future.

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OP.09

Investigating the use of JMC-chalcopyrite as in-house standard for *in-situ* Cu isotope analyses with LA-MC-ICPMS

ARAUJO DP, CRUZ LV, HAUSER N AND POITRASSON F
1 – Instituto de Geociências, Universidade de Brasília. Campus Darcy Ribeiro. Brasília-DF. 70910-900.
dparaujo@unb.br

Transition metal isotopes measured by MC-ICPMS have been increasingly used to study ore deposits. In-situ analyses can be an alternative for solution methods, but usually requires the use of matrix-matching standards to avoid matrix effects. Chalcopyrite grains from Johnson Matthey Company (JMC-Cpy) have been used by several laboratories and, compared to SRM976, δ^{65}Cu value of this material measured via solution is close to 0.06‰ (Ikehata et al. 2008, Araujo et al. 2010). Using femtosecond laser and Cu metal SRM976 as standard material, Ikehata et al. (2008) found δ^{65}Cu for the JMC-Cpy at 2.73‰ ± 0.09 and when using nanosecond laser (Araujo et al. 2010), the value was 0.63‰ ± 0.07. Here we examine the homogeneity of JMC-Cpy (Stock #42533, Lot #B27T039, supplied by Alfa Aesar) in order to use it as in-house standard. Three grains of JMC-Cpy were imaged by BSE and measured for major elements (Jeol superprobe JXA-8230) and Cu isotopes (New Wave 213 nm laser, Finnigan Neptune) in order to check their homogeneity and the presence of ex-solutions. All procedures were done in the Geosciences Institute of the University of Brasília. BSE images of three grains showed rare fine (< 40 µm) bornite exsolution (< 1%) in two grains, which can be easily avoided during in-situ analyses. Major element analyses (n=10) in three grains showed maximum standard deviation of 0.25wt% for FeO. Cu isotope analyses were also carried out along traverses both in the JMC-Cpy and SRM976 materials. Since there is no certified chalcopyrite standard for in-situ Cu isotope we applied the standard-sample-bracketing method where each material was used as standard to calculate its δ^{65}Cu to verify their homogeneity. The measurements were done in the same runs alternating both materials, which showed different drifting. The calculated standard deviation for JMC-Cpy (n=47) was 0.04‰ and for SRM976 (n=42), 0.16‰, showing that JMC-Cpy is more homogeneous than SRM976 and therefore can be used as in-house standard. Further measurements via laser and solution will be done to test homogeneity between grains from stock and to investigate the polyatomic interference of sulphur (^{32}S-^{14}N-^{16}O-^{1}H) on ^{63}Cu (Pribil et al. 2009) during in-situ analyses.

OP.10

Lu-Hf isotopes and U-Pb ages of detrital zircons from Saldania Belt, South Africa: Stratigraphic and Tectonic Implications

MIGUEL A. S. BASEI[1], HARTWIG E. FRIMMEL [2,3], KEI SATO[1], AND VINICIUS CORREA[1]
[1] Instituto de Geociências, Universidade de São Paulo, São Paulo, Rua do Lago 562, SP, Brazil
[2] Department of Geological Sciences, University of Cape Town, Rondebosch 7701, South Africa
[3] Institute of Geography and Geology, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

The Saldania Belt along the southwestern margin of South Africa shows three major tectonostratigraphic zones. The Tygerberg Zone (Tygerberg Formation) consists of a rhythmic turbiditic alternation of greywacke, silty, argillite and arenite. The Swartland Zone (Swartland Subgroup) is composed by phyllite, sericite-chlorite schist and biotite-albite schist. The Boland Zone consists of low-grade metamorphic siliciclastic rocks. The Klipheuwel Group, unconformably overlies all these tectonostratigraphic zones. In order to better assess the relationships between these tectonostratigraphic units a provenance study, using LAICPMS U-Pb age data and Lu-Hf isotopes obtained on the same detrital zircon grain was conducted.

The similarity in the youngest detrital zircon ages obtained across the three tectonostratigraphic units of the western Saldania Belt points to a similar age of deposition of all these units. The maximum age (564 ± 3 Ma) of the Tygerberg Formation (Tygerberg Zone) is within error identical to obtained (557 ± 6 Ma and 554 ± 3 Ma) in the Swartland Zone. Considering that the minimum age for both units is given by the oldest intrusive body of the Cape Granite Suite, i.e. 552 ± 4 Ma only a very short time span of a few million years remains for the deposition of these formations.

As is the case with the Nama sediments, the source of the Boland sediments was mainly from the Namaqua-Natal metamorphic belt, which forms the immediate border of the Kalahari. The youngest zircon grains with ages around 0.6 Ga cannot be sourced on the palaeocontinental margin but must come from the Pan-African orogenic belts to the west. The new zircon data for Klipheuwel Group that rests unconformably above the Malmesbury and Boland Groups indicate that the Magrug Formation must be younger than 551 Ma.

Hf data in the same zircons, show that zircons in the 0.7 - 1.0 Ga interval are responsible for the main concentration of positive eHf (0 to +5), suggesting an important mantle contribution at this time. These two age peaks show a main Hf(t) model age close to 1.5Ga suggesting that the main accretion of juvenile material to the crust occurred during the Mesoproterozoic, reinforcing the interpretation of a small Kalahari Craton contribution in the generation of Saldania Belt rocks.

OP.11

Application of Cu and Zn isotope ratios as tracers of sources and biogeochemical process in the Paranoá Lake (Brasília, Brazil)

ARAÚJO DF[1], BOAVENTURA GR[1], ARAÚJO DP[1], VIERS J[2]
[1]Universidade de Brasília (UnB) - Instituto de Geociências, [2]Université de Toulouse - Laboratoire des Mécanismes et Transferts en Géologie

Cu and Zn isotopes measurements were performed in sediment samples from the branches and the central part of the Paranoá Lake (Brasilia, Brazil) to verify their possible application as tracers of biogeochemical processes and anthropogenic influence. This artificial lake was subjected to an intense eutrophication during the last three decades due to the high human occupation of the watershed area and waste inflow derived from sewage treatment stations. A modified protocol from Maréchal et al (1999) was applied for Cu and Zn matrix separation. NIST SRM976 and JT BAKER were used as standards for Cu and Zn analyses. For mass bias correction, it was used the sample-standard bracketing method. The precisions (2σ) of the analyses were 0.08 ‰ for Cu and 0.09 ‰ Zn. δ^{65}Cu values for the reference materials BCR-2, and San Joaquin Soil were 0.29 ± 0.08 ‰ and 0.14 ± 0.08 ‰. The results of sediment samples show homogeneous $\delta^{68/66}$Zn values with a maximum variation of 0.1 ‰. In contrast, δ^{65}Cu values were heavier in the central part of the lake (-0.01 to 0.15‰), and lighter in its branches (-0.33 to -0.18 ‰). The difference of up to 0.45‰ (over 5 times the analytical error) between the central part of the lake and the branches may be associated with redox processes. The high depth (38 m), high concentration of organic matter and consequently the low rates of dissolved oxygen have probably contributed for anodic conditions in the central part of the lake. The lighter δ^{65}Cu of the sediments in the branches can be associated to recycling of leaves in the soil surface. A sediment profile from a silted up area presented depletion in δ^{65}Cu values with depth. This can be explained by fractionation of Cu through the profile due to preferential bounding of the heavier isotope during downward transport. The present work shows that applied Cu and Zn isotopic techniques are a prominent tool in limnological studies, however more data in different compartments such as soil and suspended particulate matter are needed.

OP.12

Determination of uranium isotope ratio in atmospheric deposits in Japan

KIKAWADA Y[1], OI T[1], HIROSE K[1]
[1]Sophia University - Department of Materials and Life sciences

The ^{235}U/^{238}U ratio fractionates insignificantly under natural environment. Uranium which has a different ^{235}U/^{238}U ratio from the natural one has thus resulted from anthropogenic nuclear activities. We have been trying to find the "anomalous uranium" emitted to the environments from the nuclear activities past few decades. We have found it in some atmospheric deposits having been collected monthly by Japan Meteorological Agency and archived at Meteorological Research Institute.

Atmospheric deposit samples were contacted with 4M HNO_3 at 180 °C for 15 min., and then resultant supernatants were separated from residues by centrifugation. The latter was digested with HF/$HClO_4$/HNO_3. The ^{235}U/^{238}U ratios in the supernatants and the solutions prepared form the residues were determined by ICP-QMS after the chemical isolation of uranium contained in them with the Eichrom UTEVA resin. The obtained ^{235}U/^{238}U ratios in the sample solutions were evaluated as the values with a 90% confidence limits in multiple measurements normalized to that in seawater measured at the same time.

All the deposits collected at Fukuoka, located at the northern side of the south-western Japanese Islands, since the 1960s have contained the anomalous uranium, uranium slightly enriched in ^{235}U in both of their HNO_3-soluble and -insoluble fractions. The anomalous uranium in the HNO_3-insoluble fractions might reveal that the deposits contain silicates sands transported from the Asian Continent by the prevailing westerly winds, which had fused with enriched uranium at nuclear test sites in Asia. Meanwhile, the anomalous uranium slightly depleted in ^{235}U have been found in the atmospheric deposits collected at Akita, located at the western side of northeastern Japan in the 1970s. The uranium depleted in ^{235}U had probably been injected into the atmosphere by thermo nuclear tests and transported directly through the air, since the uranium in the HNO_3-soluble fraction is more depleted in ^{235}U than the corresponding HNO_3-insoluble fraction.

OP.13

Advances in multicollector ICPMS for precise and accurate isotope ratio measurements of uranium isotopes

CLAUDIA BOUMAN*, NICHOLAS S. LLOYD AND JOHANNES B. SCHWIETERS
Thermo Fisher Scientific, Bremen, Germany (*claudia.bouman@thermofisher.com)

The accurate and precise determination of uranium isotopes is challenging, because of the large dynamic range posed by the U isotope abundances and the limited available sample material. Various mass spectrometric techniques are used for the measurement of U isotopes, where TIMS is the most accepted and accurate one. Multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) can offer higher productivity compared to TIMS, but is traditionally limited by low efficiency of sample utilisation. This contribution will discuss progress in MC-ICPMS for detecting ^{234}U, ^{235}U, ^{236}U and ^{238}U in various uranium reference materials from IRMM and NBL.

The Thermo Scientific NEPTUNE *Plus* with Jet Interface offers a modified dry plasma ICP interface using a large interface pump combined with a special set of sample and skimmer cones giving ultimate sensitivity for all elements across the mass range. For uranium, an ion yield of > 3 % was reported previously [1]. The NEPTUNE *Plus* also offers Multi Ion Counting using discrete dynode electron multipliers as well as two high abundance-sensitivity filters to discriminate against peak tailing effects on ^{234}U and ^{236}U originating from the major uranium beams. These improvements in sensitivity and dynamic range allow accurate measurements of ^{234}U, ^{235}U and ^{236}U abundances on very small samples and at low concentration. In our approach, minor U isotopes ^{234}U and ^{236}U were detected on ion counters with high abundance sensitivity filters, whereas ^{235}U and ^{238}U were detected on Faraday Cups using a high gain current amplifier (10^{12} Ohm) for ^{235}U. Precisions and accuracies for ^{234}U and ^{236}U were down to ~1‰. For ^{235}U, subpermil levels were reached.

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OP.14

Sequential voltammetric determination of zirconium and vanadium in seawater, estuaries and rivers

SCHNEIDER AB[1], DO NASCIMENTO PC[2], KOSCHINSKY A[3] - [1]Universidade Federal de Santa Maria (UFSM) e Jacobs University Bremen (JUB) - Departamento de Química (UFSM) / Earth and Space Sciences (JUB), [2]Universidade Federal de Santa Maria - Departamento de Química, [3]Jacobs University Bremen - Earth and Space Sciences

Zirconium is strongly hydrolyzed in seawater, and most likely occurs as negatively charged $Zr(OH)_5^-$ complex or neutrally charged $Zr(OH)_4^0$ complex. Zr belongs to the group of high-field strength elements, and its concentration in seawater is controlled by adsorption reactions with available mineral phases. In contrast to zirconium, vanadium is relatively poorly reactive with major dissolved cations and natural particles, which is characteristic of oxyanions. In seawater, vanadium predominantly occurs as fully hydrolyzed vanadate species such as HVO_4^{2-}, $H_2VO_4^-$, and the complex $NaHVO_4^-$. The direct determination of both Zr and V in saline matrices as seawater is problematic for most analytical methods due to either their high salt content or the organic matter. Especially the determination of the trace element Zr in seawater is difficult because of its extremely low concentration, varying from about 25 pmol L^{-1} at the surface to nearly 270 pmol L^{-1} at the bottom. Solutions for these problems have included an extensive pretreatment of the sample to concentrate the analyte and to remove the interfering dissolved salts (background). Here, the application of voltammetry showed to be an efficient alternative for the determination of Zr and V in seawater, river water and estuarine water because of a number of advantages: no necessity of out-line preconcentration, very high sensitivity, small interference of the saline media and co-existing elements, fast determinations and low costs. Thus, we propose a new voltammetric method for the sequential determination of Zr and V in the same solution after a simple step of UV-irradiation. The method is based on the adsorptive preconcentration at the Hanging Mercury Drop Electrode (HMDE) of the complexes formed between these elements and a mixture of the ligands cupferron, oxalic acid and 1,3-diphenylguanidine. Results of the Zr and V concentrations in samples from the rivers Rhine, Elbe and Weser, from their mixtures at different ratios with seawater (estuarine mixture experiment) and samples from the North sea and the Atlantic Ocean taken during the cruise ANT XXVIII/5 with the German research vessel Polarstern were obtained.

OP.15

Determination of Zr, Hf, Nb and Ta in seawater by the use of an online-preconcentration system connected to inductively coupled mass-spectrometry (ICPMS)

Poehle S[1], Koschinsky A[1], Schmidt K[1]
[1]Jacobs University Bremen gGmbH - School of Engineering & Science, SES

Zirconium (Zr), Hafnium (Hf), Niobium (Nb) and Tantalum (Ta) belong to the group of high-field strength elements (HFSE) and are characterized by their small ionic radii and high charges. In Atlantic seawater, concentrations for Zr and Hf range between 70-80 pmol/kg and 0.4-1.1 pmol/kg, respectively (Godfrey et al., 1996). An increase in concentrations with depth is observed, although these elements are defined as particle-reactive and therefore a decrease in concentration with depth is expected (Firdaus et al., 2008). There is still a lack of data concerning the distribution for Nb and Ta in seawater. Sohrin et al. reported a slight increase in concentration with depth in the North Pacific (Sohrin et al., 1998). Recently, this distribution pattern in the Pacific has been confirmed by Firdaus et al., 2011. Moreover, first insights in the fractionation of these chemical twins in seawater were provided. Therefore, further investigation is in compelling need to understand the behaviour of the HFSE in the water column. As the concentrations of Zr, Hf, Nb and Ta in seawater are very low preconcentration prior to analysis is required for most analytical methods.

A promising tool for preconcentrating Zr, Hf, Nb and Ta from seawater provides the online preconcentration system, SeaFAST, which has already been applied for the determination of rare earth elements (REE) in seawater (Hathorne et al., 2012). This system, which can be directly connected to the inductively coupled mass spectrometry (ICPMS), consists in principle of a sample loop with defined volume and a column filled with chelating resin. As two functional groups, ethylenediamine triacetic acid and iminodiacetic acid, are immobilized on a polymer backbone, the resin allows Zr, Hf, Nb, Ta, REE as well as other metals to sorb on the surface while alkaline and alkaline earth metals pass the column. First tests for elution of Zr, Hf, Nb and Ta from the resin were performed using different acid mixtures of differing molarities. Zirconium, Hf, Nb and Ta show recovery rates from 90%, 75%, 80% and 70%, respectively, using a 100 ppt standard in 0.02 M HNO_3 eluted with 0.5 M HNO_3-0.001 M HF from the column. Further improvement of the recovery rates and adjustment to seawater matrix is intended as these experiments were performed with an artificial standard. Finally, the method will be applied to samples from water column profiles taken in the Atlantic as part of the international GEOTRACES program.

Applying this online-preconcentration method no intensive laboratory work is needed for pretreatment of the seawater samples, which is a significant advantage compared to offline-preconcentration methods.
In addition, the risk of contamination is minimized tremendously. Moreover, only a small sample volume, about 10 ml, is needed to perform an analysis, facilitating sample logistics.

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OP.16

Mercury speciation with ethylation, cryophocusing, thermal gas chromatography and detection with multi-beam atomic absorption spectrophotometry

WASSERMAN, J.C.[1], WASSERMAN, MAV[2], BARCELLOS, RGS[3], SOUZA, VA[4]
[1]Universidade Federal Fluminense - REMADS-UFF, [2]Instituto de Engenharia Nuclear/CNEN, [3]Instituto Federal Fluminense - Quissamã, [4]Universidade Federal Fluminense - Dept. de Geoquímica

Mercury speciation in sediment and water samples constitute a challenge because concentrations of the different species may be very low, bellow ng levels. Many procedures have been developed to carry out mercury speciation analyses using different separation and detection procedures. For instance, GC and HPLC has proven to be reliable procedures but, due to the fact that no pre-concentration is allowed in the process, detection limits are higher than required for waters and sediments. Cryophocusing has been developed in the early 1980s and has proven to be able to carry out pre-concentrations of analytes, facilitating the analyses of contaminants like metallic mercury, mercuric mercury, methylmercury, dimethylmercury and other organic species, even in sub-nanogram concentrations. The detection procedure may also constitute a difficulty, because detectors like atomic absorption spectrophotometry is reliable, but detection levels are too high. On the other hand, atomic absorption fluorescence has very low detection levels but the procedure has to be very carefully done because interferents may cause quenching during the detection. The present work proposes the utilization of a procedure of derivatization using ethylation, hyphenated to a cryophocusing/thermal gas chromatography system and detection with a multi-beam atomic absorption spectrophotometry (Lumex). The separation procedure has already been tested by a number of authors, but the use of the Lumex mercury specific multi-bean atomic absorption spectrophotometer as a detector, permits the analysis of sub-nanograms concentrations in samples of sediments and waters. Although not tested in the present work, the procedure may also be reliable for samples of soils and organic tissues. The advantage of the developed procedure is that it can reach very low detection limits but using the technique of atomic absorption spectrophotometry that do not present quenching problems like atomic fluorescence spectrophotometry.

OP.17

Use of Direct Mercury Analyzer to assess soil Hg emissions due to forest fire in the Amazonian region

FOSTIER AH[1], MELENDEZ JJ[1], AMARAL BC[1], SANTOS JJ[2], CARVALHO JA[3]
[1]UNICAMP - Instituto de Química, [2]INPE, [3]UNESP - Guaratingueta

Several recent studies indicated that forest fires are likely responsible for the re-emission of at least part of the accumulated Hg in biomass and soil and could sharply accelerate emission and deposition cycle between terrestrial ecosystems and the atmosphere. Part of mercury release during forest fires relates to thermal desorption of mercury from soil which is strongly dependent on temperature, Hg speciation and bonding type. The aim of this work was to compare mercury burden in surface soil before and after a forest fire. Initially a careful validation of the analytical method use to determine total Hg concentration in soil samples was performed.

Six surface soil (O-horizon) samples and 6 soil samples (each one in depth 0-1, 1-2 and 2-5 cm) were collected, before and after burning in a 1-ha plot of a forest fire experiment (Acre, Brasil). Samples were analyzed by Direct Mercury Analyzer (DMA-80 Millestone). Validation parameters for analytical method were: linear range: 0.5-9 ng ($R^2 = 0.998$); LOD = 0.33 ng g^{-1}; LOQ= 1 ng g^{-1}; intraday and interday precison: 1%. Influence of granulometric composition and sample were also assessed. For accuracy, CRM NIST 2729 ([Hg]$_{certificated}$= 1400 ± 80 ng g^{-1}) and GBW-08301 ([Hg]$_{certificated}$= 220 ± 40 ng g^{-1}) yielded values of 1450 ± 70 ng g^{-1} and 225 ± 7 ng g^{-1} respectively. Robustness was also assessed by a "Youden test".

In O-horizon, Hg concentrations varied between 84±4 ng g^{-1} and 12±2 ng g-1 before and after burning, respectively. At 0-1 cm, Hg concentrations ranged 92±4 and 80±3 ng g^{-1}. The mercury burden was also calculated from Hg concentration and mass/area ratio of the samples for each sampling point.

When considering an averaged deforestation rate of 1.7 x10^{6} ha yr^{-1} for the 2000-2010 period (INPE), it was calculated that, at least, 5.0 ± 0.4 Mg of Hg could be released annually by soil due to forest fires in the Amazonian region, which is in agreement with previous data. Further studies are being performed to quantify post-burn soil Hg emission, and also Hg emissions from biomass burning.

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OP.18

High temperature acid dissolution of silicate rock samples

ALOÍSIO COTTA[1], JACINTA ENZWEILER[2]
[1]Depto de Ciências Naturais - CEUNES -UFES, [2]Instituto de Geociências - UNICAMP

Sample dissolution is a critical step for the analysis of geological materials when measurements are made using solutions. Dissolution of silicate samples is generally accomplished by combining HF with strong (and/or) oxidizing acids in closed PTFE vessels at temperatures up to 180 ºC. However the complete dissolution of refractory phases may require days of heating. Higher temperatures are expected to accelerate the reaction rate and produce faster dissolutions. To test such hypothesis, we employed the High Pressure Asher System (HPA-S) (Anton Paar, Austria), which attains temperatures up to 260 ºC when glassy carbon vessels are used in presence of HF. Several tests were made with the HPA-S for HF/HNO_3 dissolution of granitic (GSP-2 and GSR-1) reference materials (RM). Applied temperature (200, 220 and 260 ºC), addition of Mg to the test portion plus acids before dissolution, evaporation scheme (HNO_3 or $HClO_4$/HNO_3) were evaluated in order to achieve complete recoveries for 41 the trace elements determined by ICP-QMS. The reaction time in the HPA-S was fixed in three hours.

When heating at 260 ºC and using only HNO_3, recoveries varied around 60%. With the inclusion of $HClO_4$ during the evaporation step, recoveries attained ≈ 80%. In both experiments, Zr and lanthanides exhibited recoveries ≈100% indicating complete sample dissolution, however the formation of insoluble fluorides, mainly AlF_3, hampered the determination of the remaining elements. RM of basalts (BRP-1 and BCR-2) dissolved using 260 ºC and $HClO_4$/HNO_3 presented better recoveries (≈90%) than the granitic RM. Such results indicated that the higher $[(Mg+Ca)/Al]_M$ ratio favors the formation of decomposable fluorides, instead of AlF_3.

In the subsequent tests, the temperature of dissolution was lowered and Mg was added to suppress the formation of AlF_3. Most elements presented incomplete recoveries when test portions were decomposed at 200 ºC, but by raising the temperature to 220 ºC and adding suffice Mg to produce $[(Mg+Ca)/Al]_M \approx 1.2$ complete recoveries were achieved for all measurands, indicating that samples were fully decomposed and the formation of insoluble fluorides was inhibited.

OP.19

Zn-Sr-Pb isotopes as pollutant tracers in aerosol samples of São Paulo city, Brazil

SIMONE GIOIA[1], MARLY BABINSKI[2], DOMINIK WEISS[3], SPIRO BARUCH[4], AMÉRICO KERR[5]
[1]Empresa Gerencial de Projetos Navais, Centro Tecnológico da Marinha de São Paulo, SP- Brazil.
e-mail: sgioia2010@gmail.com
[2]Centro de Pesquisas Geocronológicas, Instituto de Geociências, Universidade de São Paulo.
Rua do Lago, 562. CEP 05508-080. São Paulo, SP, Brazil
[3]Department of Earth Science and Engineering, Imperial College London
[4]Mineralogy, The Natural History Museum, London, England
[5]Instituto de Física, Universidade de São Paulo, Brazil

The Zn-Sr-Pb isotope systematic could provide important information about pollutants sources and dynamics in the atmospheric environment of larger cities. To test this potential, we present recent results of the isotopic characterisation of atmospheric particulate matter collected in São Paulo City, and Mogi Valley (Vila Parisi, Industrial City - Cubatão), Brazil, during the summer and winter of 2006, using fine ($PM_{2.5}$) and coarse ($PM_{10\text{-}2.5}$) particle size fraction.

The $\delta^{66}Zn$ values range between - 0.96 and - 0.37‰ and between -1.04 and + 0.02‰ in coarse and fine particles, respectively, in São Paulo City. In contrast, in the industrial area of Vila Parisi, $\delta^{66}Zn$ are isotopically heavier and range between - 0.34 to -0.39‰ in fine and between 0.28 to -0.42‰ in coarse fractions. The $^{206}Pb/^{207}Pb$ ratios vary between 1.1357 and 1.2730 in São Paulo, and are more radiogenic (1.1698 and 1.3279) in Cubatão.

Finally, the $^{87}Sr/^{86}Sr$ ratios in aerosols (average value = 0.7138 ± 0.0008) and

OP.20

Evaluation of in situ heterogeneity of elements in solids: implication for Geoanalysis

RAMSEY MH[1], REIDINGER S[2], SOLOMON-WISDOM GO[3]
[1]University of Sussex - Life Sciences, [2]University of York - Department of Biology, [3]University of Sussex - School of Life Sciences

Analytical methods that can operate on undisturbed materials in their original *in situ* position (e.g. PXRF or microprobes) can be used to estimate the heterogeneity, as well as the concentration of an element in solids such as soil and rock. Such heterogeneity has often been seen by geoanalysts as an obstacle that must be over come to make reliable estimates of concentration, but heterogeneity can also be seen as an interesting property in its own right.

To evaluate heterogeneity, duplicated measurements have been made using an *in situ* technique, using a special experimental design, in which measurements are made across the sampling target at a range of *different* distances of separation (e.g. µm to m). Analysis of variance (ANOVA) is then often used to evaluate the heterogeneity at the various different scales. The units used to express heterogeneity are often either variance or relative standard deviation (RSD). Case studies will be described in which values of heterogeneity range from 5% to over 100% for different elements, at various scales, and where the elements been deposited by different mechanisms or have different speciation or mineralogy. Where the frequency distribution of the element concentration is not Gaussian, prior logarithmic transformation can be required. The heterogeneity is then asymmetric about the mean, and better expressed as a factor, rather than as an RSD.

The implications of heterogeneity values will be discussed, using case studies, in terms of how they can be used to:
i) express how *in situ* heterogeneity changes as a function of scale (e.g. from µm to m)
ii) diagnose the recent origin of the element (e.g. mode of deposition)
iii) predict the environmental properties of soils, such as the extent to which certain plant species can take up heavy metals.
iv) enable estimation of the uncertainty of single measurements (in combination with the analytical uncertainty)
v) design measurement (and sampling) strategies that achieve a required level of uncertainty

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OP.21

Precision, Accuracy and Some Uncertainty in Silicate Analysis

J N Walsh
Department of Earth Sciences, Royal Holloway University of London U K

Improvements in instrumentation and preparation methods have provided the opportunity to measure a wide range of major, trace and ultratrace elements in silicate samples. A combination of ICP-OES and ICP-MS techniques can be used to measure some 50-60 elements to the required levels of precision, accuracy and detection limits. For major elements a precision and accuracy of better than 0.5% RSD will be needed for high concentration elements (Si, Al etc.). For trace elements precision and accuracy at significantly higher (worse) levels will normally be acceptable. However, detection limits achieved as concentration levels in the sample will vary substantially, from a few ppm to levels below 0.1 ppm. No single instrumental technique currently available can achieve this. However, a combination of ICP-OES (good for light elements and high concentration levels) and ICP-MS (good for heavier elements and very low concentration levels) can succeed and will be discussed.

The limitations of silicate analysis data are normally considered in terms of limitations of instrumental parameters, and in some cases limitations of sample preparation methods (sample dissolution for ICP techniques). It is suggested that, excellent though this approach may be, it has somewhat distracted attention away from other limitations. The precision (and accuracy) of field sampling is rarely discussed. The quality and suitability of preliminary sample preparation (crushing and fine grinding) needs to be considered carefully. Most commonly used grinding materials introduce significant sample contamination and preferential grinding of the different mineral phases present in a silicate rock needs to be evaluated. Current grinding methods will achieve dramatically different rates of sample comminution for different minerals. Layer lattice silicate may contain very large percentages of some of trace elements in a rock sample. These minerals especially, grind down at much slower rates than other minerals (i.e. feldspars and quartz). Consequently, when a sample is weighed for analysis (using say 200 – 500 mg) the number of grains taken in the powder analysed can be unrealistically low to be representative. This issue will be considered and an attempt made to quantify the problem.

OP.22

Modifications of the IAG Certification Protocol according to recent developments in Metrology

Thomas Meisel[1] and Conny Kriete[2]
[1]Montanuniversiaet Leoben - General and Analytical Chemistry, Leoben, Austria
[2] Federal Institute for Geosciences and Natural Resources, Stilleweg 2, D-30655 Hannover, Germany

The very successful IAG certification protocol, developed and published by Jean Kane and co-workers in 2003 with modifications in 2007, was based on ISO Guide 35 1989. Since this first publication of the protocol revisions of ISO Guide 34 and 35 were published in 2009 and 2006 respectively. An adoption of new aspects is thus mandatory. First attempts to incorporate the guidelines for the calculation of contribution derived from sample inhomogeneity and from the interlaboratory comparison has led to a significant reduction of measurement uncertainties when compared to the process published by the current protocol.

Another aspect that needs consideration is the development of the past decade in the loss of variety of analytical methods applied to the analysis of geological materials. Beside XRF being a standard method, ICP-MS instruments have been improved so they now able to handle high dissolved solid content in solutions with linear calibration range that allows the determination of trace and major element contents in the same sample solution. ICP-MS nowadays can compete with XRF for most of the major element compounds. In addition through the use of collision/reaction cells molecular interferences are better under control leading to improved data for difficult to determine elements such as As, Sc, Se, etc. As a result of these developments XRF and ICP-MS are nowadays the dominating instruments for major and trace element content determinations. As these two methods are not only used for routine measurements but also for interlaboratory comparisons (ILC) which are the basis for the current certification approach problems in the comparability of the certified values may occur. In the recent ILC performed for certification purposes, the heavy rare element contents were determined solely by ICP-MS methods whereby different digestions methods are still applied such as acid digestions with HF, lithium metaborate fusions and sodium peroxide sintering. For cerium there are situations when e.g. 15 ICP-MS are compared with 1 or 2 XRF values. ISO Guide 35 does not provide explicit procedure how to deal with this situation of unbalanced data.
Answers to these challenges and consequences for the IAG certification protocol will be presented.

OP.23

Counteracting Heterogeneity in Sampling and Analysis – Theory of Sampling (TOS) vs. Measurement Uncertainty (MU)

Kim H. Esbensen[1,2*], Claas Wagner[2]
1. Geological Survey of Denmark and Greenland (GEUS), Copenhagen, Denmark. ke@geus.dk
(*presenting author)
2. ACABS research Group, Aalborg University, campus Esbjerg (AAUE), Denmark

Current measurement uncertainty approaches (MU) are assessed with respect to the complete ensemble of sources affecting the measurement process, in particular the extent to which sampling errors as set forward in the Theory of Sampling (TOS) is appropriately considered in the guides GUM and EURACHEM. All sampling steps, from primary sampling extraction, via laboratory handling, mass reduction and sample preparation procedures to analytical sample size extraction play important roles in the total uncertainty budget, which critically affects the validity of measurement uncertainty estimates. The primary sampling stage is of overwhelming importance. The so-called incorrect sampling errors (TOS) cause a sampling bias that *per force* will result in varying and unnecessarily inflated MU estimates. The sampling bias cannot be estimated however, as it is *inconstant,* and can consequently not be counteracted by a conventional statistical bias-correction. TOS therefore stipulates that the sampling bias must be eliminated for which TOS describes appropriate countermeasures. TOS constitutes the only complete, scientific theory for representative sampling, enabling appropriate treatment (elimination and minimization) of all MU sources related to sampling. While MU estimates the total measurement uncertainty, it is in reality *passive* and incomplete without TOS' *active* sampling correctness paradigm, which allows for elimination of all bias-generating incorrect sampling errors across all scales. We argue for a reconciliation of the often strongly felt worldview differences between MU and TOS, by proposing to induct TOS fully in MU. The issues addressed are illustrated with scenarios and case histories from geo-analysis.

OP.24

WDXRF Analysis of Small Samples; How Low Can We Go?

Conrey RM[1], Wagoner, LC[1], Wolff JA[2] - [1]Washington State University - GeoAnalytical Laboratory, [2]Washington State University - School of the Environment

Normal WDXRF analysis of bulk materials requires several gram samples. However, some analytical problems, for example those involving mineral or glass separates, single lithic inclusions or pumices, expensive core (e.g. ODP), meteorites, etc., do not allow use of normal sample weights. To meet these demands we are analyzing small samples down to 100 mg using WDXRF fusion methods. The smallest samples are bulked up to 200-400 mg by the addition of pure silica, and cast as 8 mm diameter fusion beads. A low dilution recipe with 2:1 Li-tetraborate is used, and both major and trace element intensities are counted on the pellets for approximately 4 hrs. Slightly larger samples, in the 600 mg to 2.0 gram range, are made with the same low dilution recipe and cast as 15 mm diameter pellets. Intensities are collected for over 2 h. Our normal 31 mm low dilution method requires 66 min, the count times on the smaller pellets are extended to retain approximately the same precision. Analysis of CRMs as unknowns demonstrates the viability of the small sample methods. Comparison of same powder ICP-MS trace element analyses also agree well. These analytical routines are not simply scaled versions of our normal method, many parameters (e.g., overlap corrections, background shapes, etc) change as a function of size and so must be established for each routine. Recently we experimented with 0.5 mm masking to see if fused pellet WDXRF calibrations could be established at that diameter. We found that all of the major and minor element calibrations were attainable, as well as the more energetic K line trace elements (we calibrated Sr as a proxy). Precision is less than with our established small sample routines but is still usable for many problems, and could be improved with longer count times and more attention to surface finish, the latter critical at this diameter. Weak L line trace element measurements would require very long count times. We conclude that there is no ultimate lower limit for WDXRF analysis, and that sample weights in the 5-10 mg range are usable, approaching the size range of laser ablation analysis but less destructive.

OP.25

The preparation and certification of in-house reference materials for XRF calibration

Loubser M[1], Crook C[2], Nyembe B[2] - [1]PPC Cement - Group Quality Sevices, [2]PPC Cement - Group Laboratory Services

Within the PPC group analytical data collected over a period of time is evaluated to ensure that the XRF calibrations cover the different analytical ranges for different elements and materials analysed in a specific factory. This has been a challenge to adhere to, due to the difficulty in obtaining suitable reference materials. Analytical data are even more crucial when the process goes out of specification and it is in these instances that routine calibrations often do not have the range to accurately analyse the "outliers".

Commercially available certified reference materials (CRM's) are limited in number and range for cement raw materials and clinkers. Even cement reference materials do not necessarily cover the specific products produced in the group's factories. In the past reference materials were collected and prepared for each factory individually but this made it very difficult to obtain a decent analytical range. A cement kiln for instance is run along strict operational parameters and the product composition is thus tightly controlled making it difficult to obtain concentration ranges on the constituent elements. The same applies to raw materials where a particular limestone quarry has a specific compositional finger print.

Because of tight turnaround times for production control analysis, pressed powder briquettes are routinely used resulting in additional uncertainty arising from sample preparation and mineralogical matrix effects.

This paper describes protocols followed in a project launched to prepare in-house reference materials.

Firstly raw materials, intermediate products and final products were collected from all the different factories. The materials were then homogenized and split followed by homogeneity testing. Samples were then taken and prepared for duplicate XRF analysis by fused bead method against a calibration set up with CRM's.

Some samples were also outsourced to other XRF laboratories for comparative analysis along with some samples being analysed using ICP-OES. A further evaluation of data was done by preparing pressed powder pellets and setting up calibrations using the fused bead data obtained to ensure linear fit. Outliers were re-analysed. During implementation at the factories, any outliers were identified and re-analysed ensuring proper certification at the end of the process.

When calibrating the factory spectrometers with the combined set of reference materials the necessary analytical range was obtained, and mineralogical effects due to locational differences and kiln conditions did not prove to be a problem.

OP.26

An assessment of analytical performance in the routine analysis of silicate rocks: An analysis of data submitted by geochemistry laboratories participating in the Geo*PT* proficiency testing programme – 2001 to 2012

Philip J. Potts and Peter C. Webb
Faculty of Science, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK
Phil.j.potts@gmail.com

The Geo*PT* proficiency testing programme was initiated in 1996 by the International Association of Geoanalysts to provide an opportunity for laboratories worldwide to evaluate their performance in the routine analysis of silicate rocks. Participating laboratories are invited to contribute analytical data on samples distributed as unknowns twice a year and to respond to their corresponding '*z*-scores', which are a measure of analytical performance for the individual analytical results submitted to that round. *Z*-scores in the range $-2<z<+2$ are considered to be satisfactory; but when *z*-scores for individual analytes exceed this range, laboratories are advised to examine their methodologies for unsuspected analytical bias. The overall aim of the programme is to allow participating laboratories to assess the quality of their data in comparison with their peers and to provide a way of improving the overall quality of data produced by the sector over a number of rounds in the expectation that individual laboratories will respond to unsatisfactory *z*-scores. A large body of data has been accumulated in the reports that have been produced over the last 16 years. This paper presents an analysis of Geo*PT* proficiency testing data from Geo*PT*10 (2001) to Geo*PT*30 (2012) with the aim of evaluating trends in data quality and identifying elements for which analytical performance appears to fall below expectations, indicating areas for further investigation and possible development by the geoanalytical community.

OP.27

Quality Assurance in the U.S. Geological Survey Energy Geochemistry Laboratory

Marshall BD[1] - [1]U.S. Geological Survey - Energy Resources Science Center

The United States Geological Survey (USGS) Energy Resources Program provides data to help understand the formation, accumulation, occurrence, and alteration of geologically based energy resources; to conduct scientifically robust assessments of those resources; and to assess the impacts of energy resource use on environmental and human health.
In many laboratories, Quality Assurance (QA) requirements stem from regulations or from the desire to meet certain accreditation standards. In contrast, the USGS, in order to maintain high-quality standards, developed requirements set forth in the USGS Fundamental Science Practices (USGS Circular 1367). These practices set forth four requirements that are directly applicable to the laboratory environment: 1) consistency, objectivity, and reproducibility of data collection activities, vetted through a peer review process; 2) documentation of methods used to collect data in large quantity or frequency; 3) publication of methods in accessible form; and 4) traceability of collected data to national and international standards and protocols.

The Energy Resources Program Geochemistry Laboratory (EGL) recently revised its QA manual (http://energy.usgs.gov/GeochemistryGeophysics/GeochemistryLaboratories.aspx) in order to be fully compliant with the requirements set forth in the USGS Fundamental Science Practices (FSP). The manual consists of 13 sections; sections on methods and records are key to addressing the FSP requirements. The methods section sets forth a standard outline for method documentation, including requirements for revision history and for associating the documents with collected data stored in the EGL Laboratory Information System (LIMS). The method documents must include information on calibration and quality control (QC) samples, the acceptance of data, the handling of data from instrument output to LIMS, and follow an accepted review and approval process. All data in the LIMS are validated after entry by the appropriate analyst prior to final verification by QC staff. Although the LIMS enhances record-keeping in the EGL, the records section of the QA manual requires that instrument logbooks and laboratory notebooks are also maintained. Other sections of the QA manual cover the organization and responsibilities of personnel and a requirement to maintain a corrective action program that facilitates tracking and resolution of problems. EGL staff are tested in performing new methods by analysis of blind reference materials. Participation in applicable proficiency testing programs is documented by QC staff. It is expected that external audits of the EGL QA program will be conducted at regular intervals in order to confirm compliance and improve on the policies and procedures set forth in the QA manual.

OP.28

Quality Assurance in the European Geochemical Mapping Project GEMAS

Cornelia Kriete[1], Clemens Reimann[2], Manfred Birke[1], Alecos Demetriades[3], GEMAS Project Team[2]
[1]Federal Institute for Geosciences and Natural Resources, Stilleweg 2, D-30655 Hannover, Germany
[2]Geological Survey of Norway (NGU), PO Box 6315 Sluppen, N-7491 Trondheim, Norway
[3]Institute of Geology and Mineral Exploration (IGME), Spirou Louis Street 1, 13677 Acharnae, Greece
E-mail contact: cornelia.kriete@bgr.de

Quality assurance is one of the keystones to the success of any large scale geochemical mapping project requiring harmonized data. It has to be assured that sampling and analytical precision are sufficient not to conceal regional differences and to proof trueness and comparability of the mapping data.

Therefore a set of stringent quality control (QC) measures were introduced into the analytical program of the GEMAS (Geochemical Mapping of Agricultural and Grazing Land Soils) project including field duplicates, analytical duplicates, insertion of two project quality control materials (Ap and Gr) as hidden internal references between true samples, and randomization of all samples prior to analysis. The within-lab-reproducibility of QC data for the QC materials Ap and Gr is generally good, but strongly dependent on the analyte. The nested design of duplicate field and duplicate analytical samples allowed carrying out a statistical analysis of variance (ANOVA) to identify the relative contributions of regional, sampling and analytical variances. The ANOVA demonstrates that the technical variability is low enough to detect regional differences in geochemical maps.

For confirmation of trueness and comparability a proficiency test (PT) based on the project quality control materials was performed in 2011. In total 21 institutions from 16 countries submitted analytical data, providing 36 data sets. The mean values from QC analyses were treated as "normal participants". Robust statistics (Hampel estimator and Q-method) were used to estimate assigned reference values and reproducibility standard deviations for 95 total and aqua regia (AR) extractable element concentrations and LOI for both reference samples. Horwitz ratios (HorRat) as indicator for the proficiency test performance reveal a large uncertainty component introduced by the AR extraction step especially for main components, which are not covered by the scope of the relevant ISO standard.

For laboratory assessment zu scores were calculated. For all total element contents and most of the AR extractable concentrations zu-scores of the QC data are within the tolerance limits. Exceptions are especially those components with a general poor reproducibility in the PT. Thus the trueness and comparability of the mapping data could be confirmed.

OP.29

USGS/EPA development of bioavailability reference material SoFC-1 used in the toxicological evaluation of Arsenic and Lead

S. Wilson[1], S. Morman[1], L. Choate[1], K. Bradham[2], M. Burgess[2]
1. U.S. Geological Survey, 2. U.S. Environmental Protection Agency

In a collaborative study between the U.S. Geological Survey (USGS) and the U. S. Environmental Protection Agency (EPA) a specialized soil reference material (SoFC-1) was requested which would contain concentrations of arsenic and lead at 600 and 6000 ppm respectively. The goal of the study was to produce a long term supply of contaminated soil that would assist investigators in evaluating the human health issues associated with contaminated waste sites. Starting material was collected from the EPA hazardous waste site located along Flat Creek near the town of Superior, MT and blended with baseline soil from the area to achieve the desired element concentrations. SoFC-1 was examined for total, acid extractable and simulated gastric fluid (SGF) extractable elemental concentrations. Acid extraction studies utilized EPA's 3050 and 3051 procedures which are mild nitric acid/peroxide extractions designed to mimic potential leachability under long term environmental conditions. Laboratory SGF studies utilized a solution of HCl (0.03M) and lysine (0.4M) designed to mimic the leachability of trace elements in the human digestive system. Total and extractable element data were then compared to an in vivo study conducted by EPA.

Total element results indicates that SoFC-1 contains elevated concentrations of Ag (50 ppm), As (700 ppm), Pb (6400 ppm), Sb (1000 ppm) and Zn (8900 ppm) as well as moderate concentrations of Cd (55 ppm) and Hg (14 ppm). 3050 extraction results reveal nearly complete extractions of these metals from the solid. Gastric extraction data show percent extraction ranging between 7% (As) and 58% (Pb). Results will be discussed in terms of the suitability of SoFC-1 as a biogeochemical reference material and how extraction results correlate with animal uptake studies.

OP.30

The preparation of three polluted area soils and ore mien waste reference materials

Dai-hong LUO, Lin GUO, Wei ZHOU, Huai-ying ZHAO, Yue-jin DENG, Lu GAN, Jun-yu XU, Peng QI
National Research for GeoAnalysis, 26 Baiwanzhuang Street, Beijing 100037, CHINA
Email: dluo@cags.ac.cn

Three polluted area soil and ore mine waste reference materials, GPS-01, GPS-02, GPS-03 were prepared by National Research Center for GeoAnalysis, China. Two of the candidate samples were collected in a Pb-Zn ore mine tail sediment and in the polluted area field in Shaoguan, Guangdong Province respectively. The third candidate sample was sampled from the flooded area caused by the collapse of an ore tail on 8 September 2009 of an iron mine in Xiangfeng, Shanxi Province.

The samples were naturally dried and passed through 5 mm screen to remove stones. The three candidate reference materials were ground to -200 meshes. The homogeneity of the candidate samples was found adequate by using F-test. A two-year stability tests show that the samples were stable during the time. Ten Chinese laboratories participated in the analysis program and more than 50 elements will be certified for each of the candidate reference material. Most of the elements were determined by means of ICP-AES, ICP-MS, XRF, AAS, AFS and other methods.

The candidate reference materials will be useful for use in calibration and quality control in the analysis of samples collected for soil quality investigation and evaluation project in China.

ABSTRACTS

POSTER SESSIONS

PT.01

Specificities in measuring composition of gold and silver formations by EPMA within hypergene zones

Liudmila Pavlova, Raisa Kravtsova, Yulia Tarasova
Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences,
[1]a Favorsky Str., Irkutsk, 664033 Russia, pavpla@igc.irk.ru

The EPMA technique is elaborated to determinate of Au and Ag composition in derived circumstances. The silver-containing formations are not stable during the electron probe action. The change of the silver intensity in accordance with the beam power densities was chosen as the criterion to select optimum conditions for analysis. Thus the beam power densities >2.55 µW/µm^2 are unacceptable for silver-containing samples. The metrological testing of the elaborated technique was carried out using reference samples containing silver. The quality of all available results complies with the "applied geochemistry" category of performance (category 2).

These techniques are applicable for prospecting as the criteria for a perspective evaluation of geochemical anomalies.

Fine grains collected from heavy fraction of loose sediments were investigated using microprobes JXA8200 and Superprobe-733 (JEOL Ltd, Tokyo, Japan). When we study the anomalies we found that Ag-Au intermetallic compounds are very rarer. They are basically single fine grains of electrum. In addition to proper mineral mode of occurrence, Au concentrations are found in Fe and Mn hydroxides, destructed pyrite and chalcopyrite grains and silver minerals. Obtained data indirectly indicate the existence of the colloid-dispersed and the so-called "bound" with sulfides (sorption? structural?) mode of gold.
Akantite, sternbergite, Ag sulfosalts, native Ag are predominant among Ag minerals. Silver minerals are differently corroded and look like hypergene ones. Native silver includes fine-dispersed particles. Among Ag sulfosalts only pyrargyrite has been found. Silver segregates when silver-containing polymetals and chalcopyrite are decomposed in hypergene conditions. It is confirmed by the shape of microinclusions of minerals as the teardrop-shaped margin around sulfide grains – the margin around the chalcopyrite grain contains mainly the mixture of fine teardrop-shaped grains of native Ag and sternbergite.

This work was supported by the RFBR and SB RAS (grants 11-05-00214 and 48).

PT.02

Heavy metals and As distribution in marine sediments of Tabatinga Bay, Caraguatatuba, Brazil

Camargo, DP[1], Ferreira PAL[1], Ribeiro AP[1,2], Figueira RCL[1]
[1]Instituto Oceanográfico / Universidade de São Paulo, [2]Universidade Nove de Julho

Sediments are the main receivers of heavy metal introduced in the aquatic environment due to anthropic activities. These pollutants reach the marine environment through river discharge, amongst other processes, modifying water and sediments quality in coastal regions. Tabatinga Bay stands out for its many impacts caused by state occupation, marinas installation and increase in watercraft number and nautical equipment. Thus, chemical analysis and heavy metal (Al, Cr, Cu, Fe, Mn, Ni, Pb, V, Sc, Zn e Sn) and As determination through the means of ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) were conducted to assess their concentration levels and spatial distribution in Tabatinga Bay. These elements concentrations were below the levels established by Brazilian and international legislations. The lowest levels of the metals analyzed were located within Tabatinga River, with higher concentrations near the mouth of the river and within the lower Bay.

PT.03

Modes of gold occurrence in the ores of gold-silver deposits (North-East Russia)

Raisa Kravtsova, Vladimir Tauson, Liudmila Pavlova
Institute of Geochemistry, Siberian Branch of the RAS,
[1]a Favorsky Str., Irkutsk, 664033 Russia, pavpla@igc.irk.ru

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Investigations were performed at Au-Ag deposits of Dal'nee, Quartz Sopka, Dukat and Rogovik. The modes of occurrence (MO) of gold were studied by the method of electron probe microanalysis with. The gold contents in pyrite were determined by atomic absorption spectrometry. The method of statistical sampling of analytical data for single crystals has been developed and used to estimating the structurally bound part of Au concentration in minerals.

It is shown that the main MO of gold in ores is the dispersed gold and fine gold. The native gold is mainly represented by electrum. The fineness varies from 200 to 750. Gold is accumulated in sulfides, mainly in pyrite. The native gold from volcanogenic deposits Dal'nee and Quartz Sopka constantly contains Te, Bi and S, volcano-plutonogenic Dukat and Rogovik – Te, Hg and Sb. In the last case Hg dominates among admixed elements, up to the formation of amalgams AuHg - AgHg. The zonality in MO of gold due to different physical-chemical parameters of ore deposition processes at different depths is observed.

The study of gold MO in pyrites of ore veins allowed estimating two main forms: a surface-related form in nonautonomous phase (NAP) and a structurally bound gold in the volume of a crystal. The fraction of structural Au in pyrite from veins is not more than 15% and amounts ~0.1-0.5 ppm. Thus, the nature of high contents of gold in pyrite is basically related to the crystal surface. The high Au contents in NAP are due to extremely elevated coefficient of Au distribution between crystal and solution as compared to structural mode – up to 3000 times. The procedure undertaken to separate Au modes and estimate structurally bound constituent allowed obtaining of information about probable Au concentrations in ore-forming fluids.

This work was supported by the RFBR and SB RAS (grants 11-05-00214, 12-05-00144 and 48).

PT.04

Evaluation of LIBS for elemental microanalyses of clay-bearing material

Cousin[1], Berger G.[1], S. Maurice[1], O. Gasnault[1], O. Forni[1], Wiens R.C.[2]
[1]IRAP, Université Toulouse, France, [2]Los Alamos National Laboratory, NM, USA

Stand-off remote sensing analysis provides new perspectives for exploring rugged environments using Laser Induced breakdown Spectroscopy (LIBS). As an example, NASA's Curiosity rover (MSL mission, arriving at Mars in August 2012) carries the ChemCam laser probe that can perform chemical microanalyses by laser spectroscopy at distances of up to 7 m from the rover. In the present study we used a 7 mJ IR laser probe coupled with a 240-910 nm spectrometer, similar to the ChemCam flight model, to test the ability of LIBS in space exploration to recognize altered rocks from pristine basalt.

LIBS is well known to be sensitive to numerous parameters, and analysts have developed methods based on multivariate analysis of the whole spectra to obtain abundances of multiple elements simultaneously. By contrast, we used here peak area ratios to determine the elementary composition, including oxygen, of clays, oxide and few ceramic samples. Pure clays and oxides were conditioned as frits and were used to calibrate the relationships between the peak area ratio and elemental ratio. For these tests we considered the major components Si, O, Al, Fe, Mg, Ca only. A set of equations was completed with the assumption that the sum of the analyzed elements matches the total composition of the sample. This is obviously not true for clay minerals or altered basalts where OH, H_2O, SO_4, CO_3 increase the relative abundance of oxygen with respect to a mafic composition. This deviation is quantified in the ratio O/Scations which differs from 1 for oxidized and hydrated samples, or sulfate-carbonates bearing samples.

The deviation from mafic composition using the O/Si ratio, was used as indicative of the clay structure. Different composition fields can be distinguished, corresponding to different clay structures. Our measurements suggest that this method may constitute a rapid assessment of the mineral composition of clay-rich samples during field or space exploration.

PT.05

Study of the granulometric composition of rock reference materials by EPMA

Liudmila Pavlova and Elena Anchutina
Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences,
[1]a Favorsky Str., Irkutsk, 664033 Russia, pavpla@igc.irk.ru

The aim of the present work is to study the granulometric composition of the reference materials of granite SG-4, synnyrite SSn-1 and svyatonosite SSv-1 developed by Institute of Geochemistry (Irkutsk), Siberian Branch of Russian Academy of Sciences. Researches were performed using electron X-ray microanalyzer JXA8200 (JEOL Ltd, Japan).

The samples of reference materials were prepared for study via gluing the arbitrary selected amount of the rock's material on the two-sided adhesive carbon tape. The images of particle distributions for reference materials and their separated fractions were obtained in back scattered and secondary electrons with zoom factors of 40, 300, 1000 and 2500-power. Visual differences of the surfaces examined were not revealed. It shows that rock grinding of granite SG-4, synnyrite SSn-1 and svyatonosite SSv-1 is identical.

Particles of all reference materials have mostly the angular irregular shape. Perhaps the minerals composing the reference materials are destroyed at grinding basically along cleavage planes. The linear sizes of particles, as a rule, do not exceed 80 μm. However the extended particles are found as well; the width and height of these particles are not more than 80 μm, while the length exceeds this value. The large particles have the silicate composition.

The reference materials contain the rounded particles as well. The diameter of spherical particles ranges from the tenth shares of micron up to 10 μm. The chemical composition of these "balls" corresponds to the composition of the silicate minerals too. Probably these spherical particles are formed because there is a local overheating of a rock during its grinding by abrasion. All particles from micron-size till biggest are covered by finer dust-like particles. The particles containing heavy elements are basically concentrated in the fine fraction of reference materials (<40 μm).

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PT.06

Portable XRF Calibration using Influence Coefficients

Conrey RM[1], Wolff JA[2], Seyfarth A[3], VanHoose A[2], Goodman Elgar M[4], Bettencourt N[4], Boschmann D[5], Werling K[2]
[1]Washington State University - GeoAnalytical Laboratory, [2]Washington State University - School of the Environment, [3]Thermo Fisher Scientific, [4]Washington State University - Department of Anthropology, [5]Oregon State University - Department of Geosciences

Calibration of portable XRF devices has become important due to the recent explosion in interest and wide range in application of these devices. Current calibration methods invariably employ proprietary fundamental parameters (FP) software or multivariate statistical analysis (MVA). Contrary to normal practice for most analytical instrumentation, with the exception of one manufacturer, users have little or no control of instrument parameters or calibration choices. In addition, there are few solid certified reference materials (CRMs), so many calibrations used for solid analysis rely upon powder CRMs. Consequently, there is often wide disparity between data obtained with different instruments and also between PXRF data compared to more precise bulk analytical data (WDXRF, EDXRF, INA, ICP etc). Most proprietary analytical methods rely upon the use of filters to optimize signal for a few elements of interest, thus necessitating the use of MVA or FP calibrations because insufficient matrix elements are detectable. In our work we decided to use unfiltered spectra so that enough matrix element intensities could be gathered to make approximate absorbance and secondary enhancement corrections using influence coefficients. We find this strategy gives results equal or superior to published FP or MVA methods, and agreement between same sample WDXRF and PXRF data for our calibrations is very good. The method is theoretically superior to MVA because all of the spectral overlap and matrix corrections are based upon the sample and detector X-ray physics, not just statistical constructs. And unlike MVA calibrations, influence coefficient calibrations can be used across a broad range of matrices and more confidently extrapolated outside the calibration range. To date, we have constructed calibrations for powdered rhyolite pumice, powdered basalt, fine grained (polished flat surface) volcanic rock of any composition, diverse Bolivian archaeological sediment, and heavy element contaminated soil. As with any analytical method, sample preparation is critical for good results, and sample material must be matched to the calibration material, e.g., solid to solid, or powder to powder. Manufacturers of these devices should allow full instrumental control as options, otherwise PXRF data may never be regarded with the same confidence as other bulk analytical data.

PT.07

Study of Soil Profiles in Irkutsk Region by XRF and EPMA

Tatiana Aisueva, Olga Belozerova
Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Irkutsk, Russia
* Presenting author: e-mail: aisu@igc.irk.ru

Soils in the Irkutsk region vary widely. As a result of anthropogenic influence, wind and water erosion and climatic conditions, soils are subject to considerable changes in both chemical and mineral structure. Therefore, at the ecogeochemical studies of territories it is necessary to have rather full information about chemical, phase and mineral composition of soils. The promising analytical methods for solving these tasks are nondestructive methods such as X-ray fluorescence analysis (XRF) and X-ray electron probe microanalysis (EPMA).

This paper presents the results of soil profiles study in the Irkutsk region using XRF and EPMA. The objects of study were the three of soil profiles. The depth profiles reached up to 100 cm. Concentrations of major and trace elements were determined by XRF. The measurements were performed using wavelength dispersive XRF spectrometer (S4 Pioneer, Bruker AXS), equipped with rhodium X-ray tube. The loss on ignition in the samples varied from 7 to 30%.

The obtained XRF data show features of elements distribution in different soil horizons. For example, the accumulation of Pb, Zn, and Mn is observed in the horizons enriched by the organic matter.

The phase mineral composition of soil from horizons was studied by EPMA. The investigations were performed applying Superprobe JXA-8200 (JEOL Ltd, Japan) microanalyzer. The phase composition of soils, shapes of phase separation, the structure of surface and size distribution were estimated using the scanning electron microscope in secondary and back scattered electrons. The chemical composition of phases as individual particles was determined using energy-dispersive spectrometer.

The results of investigation obtained by EPMA allowed the changing of phase mineral composition from horizons in soil profiles The upper horizons are characterized by more various compositions of mineral phases, presented as silicate minerals, carbonates, phases with carbon compounds, metallic granules and spherules. The phases presented mainly by silicate and ore minerals dominate in the middle and lower horizons.

Thus, the detailed investigation of soils in the Irkutsk region by XRF and EPMA allows receiving the complete information about the state of the soil cover during environmental and geochemical research.

PT.08

Investigation of Be-bearing Silicate Glass as Laboratory Reference Sample at X-ray Electron Probe Microanalysis of Silicates

Olga Belozerova, Mikhail Mikhailov, Tamara Demina
Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Irkutsk, Russia
* Presenting author: e-mail: obel@igc.irk.ru

The reliability and precision of results obtained by any relative method of analysis depend on the used reference samples. Method of X-ray electron probe microanalysis (EPMA) allows determining the contents of the elements in a wide range of atomic numbers and concentrations. The deficiency and occasionally the lack of international and state reference samples, necessary for solving of certain analytical tasks, motivate the actuality to make the multicomponent laboratory reference samples, homogeneous on macro- and micro-levels and adequate by composition to investigated materials.

The results of homogeneity estimation of Be-Mg-Al silicate glass and the opportunity to use it as laboratory reference sample at EPMA of silicates and oxides are presented in this work. The glass was synthesized in the laboratory of monocrystal physics (Institute of Geochemistry, SB RAS). The samples were analyzed via Superprobe JXA-8200 (JEOL Ltd, Japan). The intensities of elements analytical lines were measured using wavelength-dispersive spectrometers. Matrix corrections and calculation of element contents were done by the ZAF approach applying the software of quantitative analysis for microanalyses.

The homogeneity of Be-silicate glass was estimated from the distribution of Mg, Al and Si on surface of sample in X-rays of element characteristic radiation and back scattered electrons applying scan electron microscope. The homogeneity on macro- (10-100 μ) and micro- (1-10 μ) levels was studied both in the separate parts of sample and throughout the entire sample analyzed and evaluated applying the scheme of one-way and two-way dispersion analysis.

The application of Be-silicate glass as reference sample was tested on the international reference glasses and laboratory reference samples of minerals with a known composition. Obtained experimental data on the metrological characteristics correspond to the "applied geochemistry" type of analysis (second category) and showed that Be-silicate glass is appropriate to use as laboratory reference sample at EPMA of silicates and oxides.

Application of Be-silicate glass as reference sample allowed obtaining satisfactory data on the composition at EPMA of some minerals: cordierite, beryllium indialite, beryl, also of metastable phases: chrysoberyl, sapphirine, compounds with structure β-quartz and petalite.

PT.09

Investigation of Soil and Snow Cover Sediments in Baikal Region by X-ray Electron Probe Microanalysis

Olga Belozerova
Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Irkutsk, Russia
* Presenting author: e-mail: obel@igc.irk.ru

The industrial centers have deleterious effect on the environment changing its chemical and physical characteristics as a result of intensive productive activity. Therefore, environmental research of different natural media is an actual task today. Soil and snow covers are informative indicators of the environment pollution. In this connection, it is very important to have information both about the chemical composition and the substance phase distribution on micron level, shape phase separation, sizes, structure of surface. Electron probe microanalysis (EPMA) is one of perspective methods for solving these tasks.

The complex EPMA investigation of soil mineral component and snow cover sediments was conducted in Baikal region with the aim of environment pollution estimation. The samples for research were collected from regions with various man-caused loading degree.

The EPMA techniques are developed for soil and snow applying Superprobe-733 and Superprobe JXA-8200 (JEOL Ltd, Japan) devices. Sample preparation for analysis, the selection of standards and choice of optimum conditions for measurements and estimation of metrological characteristics are considered. The phase composition, surface of particles, morphology of separate phases, sizes and homogeneity of their distribution were studied using a scanning electron microscope.

The chemical composition in soil mineral components and snow cover sediments was determined using energy-dispersive and wavelength-dispersive spectrometers. The relative intensities in determined element contents were calculated by the ZAF-, PAP-approaches and from the biexponential model for the function of X-ray radiation distribution with the depth of the sample. The chemical compositions of soil and snow covers were compared.

The obtained results of investigation allowed determining the regions with different levels of anthropogenic loads, which differ in proportion of natural and man-made origin particles, detecting the changing of phase and chemical composition from regions, observing the dynamics of common level accumulation of anthropogenic component from background regions to industrial regions with high man-caused loading degree, depending on specific character and increase of industrial activity.

Thus, the data of EPMA investigation of soil and snow covers, as indicators towards the change of industrial situation in region, allows estimating environment pollution, its evolution and evolution of the background.

PT.10

A new LA-MC-ICP-MS (Neptune) multi user laboratory at State University of Rio de Janeiro

MC Geraldes[1], AD, Tavares[2], AC, Jardim[3]
[1]Universidade do Estado do Rio de Janeiro - Departamento de Geologia Regional e Geotectonica, [2]Universidade do Estado do Rio de Janeiro, [3]Thermo Scientific

A new mass spectrometry laboratory with plasma ionization, multi collector detector and laser ablation (LA-MC-ICP-MS) is being implemented in UERJ. The central equipment is a Neptune Mass Spectrometer with high efficiency in the composition analysis of very low elemental levels samples allied to a very good accuracy in isotopic analysis. These achievements are based on a sophisticated machine architecture which consists in a plasma ionization chamber coupled to a magnetic separator and detector consisting in nine Faraday collectors, eight independently adjustable and a fixed one.

Inductively coupled plasma mass spectrometry has been developed by researchers in earth sciences. Important technical improvements have been incorporated. Laser parameters as wavelength and beam profile were optimized and camera sample holder and positioner were enhanced.

Samples may be introduced into the plasma via laser ablation with an excimer laser (ArF), with high energy pulses that allow heating and ablation of opaque and very refractory materials. The analyzer is constituted by a magnetic sector which scales continuously allowing the dispersion of a high voltage accelerated ion beam source. The fully computer driven double focusing system enables the optimization of ions beam, resulting in high transmission capacity and low mass discrimination. The system of eight mobile detectors plus a fixed central allows high mass accuracy simultaneously. Detection includes SEM (secondary electron multiplier) ion type detectors, a preamp circuit system and a device for discriminating and counting ions. A system of multiple ion detectors type MIC (Multiple Ion Counting Device) is employed with a multiple array of *channeltrons*. Such an arrangement may be configured for using to simultaneous detection of weak signals from low abundance samples. This new laboratory is based on the need to support the development of new technologies and innovations through the interaction among different field researchers.

PT.11

The application of database technology on the management of original data for reference material preparation

Dai-hong LUO
National Research for GeoAnalysis, 26 Baiwanzhuang Street, Beijing 100037, CHINA
Email: dluo@cags.ac.cn

A database and data processing system was developed at the National Research Center for GeoAnalysis in China and applied to the whole process of Reference Material preparation. The system was developed under Microsoft Windows Operating System, using MS SQL Server or MS Office Access as the database. The provided tools are for homogeneity test, stability test, data normal distribution test, multi-laboratory evaluation, data processing and analytical methods statistics and can meet the requirements of data management and processing during the production of reference materials. This database applicative of the reference material management information system consists of the following modules:

- research project management
- candidate reference material sample management
- user management
- co-operation laboratory management
- system log file
- sample stability test
- homogeneity test data import/export and processing
- evaluation data import/export and processing
- outliers with Grubbs and Dixon tests
- data distribution test—Skews-Kurt, Shapiro-Wilk, D'Agostino
- calculation of multiple statistics parameters such as arithmetic mean, geometric mean, standard deviation, median, modified median, mode, mode V, Trimean, 1/4 trimmed mean, Gast Median, and others
- original data report
- statistics parameter data report
- analysis method charts by sample and element

The system was implemented at National Research for GeoAnalysis and Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences and some other laboratories in China as a basic tool for the preparation and management of reference materials preparation.

A database was compiled with more than 30 reference materials produced in recent years in China. The database contains very detailed information for each reference material, including sample description, sampling location and year, sample type, year of certification, laboratories contributing with analytical data, data provided by each laboratory including detailed parallel analysis data, analytical methods and other related information. The database can provide data support for further investigation and the modification of certified values of reference materials in the future.

PT.12

The synthesis of cutting-edge laboratory methodology and highly effective analytical service - Resource analytics at the newly founded Helmholtz-Institute Freiberg for Resource Technology (Germany)

Renno AD[1], Gutzmer J[2], Merchel S[1], Möckel R[1], Krause J[1], Rugel G[1], Haser S[1], Ziegenrücker R[1], Michalak PP[3]
[1]Helmholtz Institute Freiberg for Resource Technology - Department of Analytics, [2]Helmholtz Institute Freiberg for Resource Technology, [3]TU Bergakademie Freiberg - Institute of Mineralogy

Based on an initiative of the German Federal Government the Helmholtz Institute Freiberg for Resource Technology (HIF) is being established jointly by the Helmholtz-Zentrum Dresden-Rossendorf and the TU Bergakademie Freiberg. The new institute is to make a vital contribution towards implementing the national German strategy on raw materials. These visions and aims form the intellectual basis for the scientific work at the HIF:

- New technologies for utilization of mineral and metal containing resources from complex domestic and foreign deposits
- Contribution to global environmental protection by means of material and energy efficient extraction and use of raw materials
- Economic networks between Germany and resource countries based on sustainable technologies provided to German industry by the Helmholtz Institute (technology in exchange for access to raw materials)
- Training of new generation of highly qualified academic and technical staff for German industry and academia

The chemical and phase analysis of all natural and synthetic materials involved in the supply chain, named as resource analytics, is one of the backbones of the HIF. During implementation of the Department of analytics we embark on the following strategy:

- Concentration of all competences and capacities in one department available to all other departments
- Avoiding isolated applications
- Strict integration of the analysts during acquisition and design of projects
- Consistent integration of further development of laboratory methodology into scientific projects of the respective departments.

We describe the rationales and present first results of our landmark projects in resource analytics:

- High-speed PIXE of natural and synthetic materials
- Super-SIMS
- Automated mineralogy
- Reference materials for microanalytical methods and demonstrate the interplay with the common projects of the HIF.

PT.13

Mineralogical alteration in soil submitted to different uses

Jessé Rodrigo Fink[1]; Alberto Vasconcellos Inda[1]; Victor Hugo da Silveira[1]; Matheus Leonardo Correa[1]
[1]Universidade Federal do Rio Grande do Sul, Departamento de Solos, Porto Alegre, Rio Grande do Sul, Brasil.

Land use changes affect matter fluxes in the pedoenvironment and may alter the soil clay fraction mineralogy. With the use of X-ray diffraction such changes in soil mineralogy can be observed. The study looked at the mineralogical composition of an Argissolo Vermelho submitted to different uses and managements. Soil samples were collected in the 0.00-0.025 m layer of a pristine area (CN), of paddock (PT) and cropland uses, under the no-till management systems with poultry bed litter (PDCC) and without poultry bed litter (PDSC). Non-oriented slides were prepared from samples of deferrified clay fraction of each soil use/management and the following treatments applied: saturation with K at 25, 110, 300 and 550 ºC and saturation with Mg at 25 ºC and Mg+glycerol. X-ray diffractograms was obtained within 2 to 40°2θ (slides of K at 25ºC) and 2 to 15º 2θ (all other treatments of K and Mg). The main minerals of the deferrified clay fraction common to all uses/managements are kaolinite, quartz and anatase. In the CN, minerals 2:1 were found with Al polymers between the layers and minerals of the micaceous group. PDSC had a similar composition. On the other hand, in PDCC the absence of micaceous reflection and alteration of the kaolinite peak at low angles suggests the alteration of micaceous minerals to interstratified 2:1 and 1:1 clay minerals. In the PT, the minerals were altered more intensely than in the other managements and only intense reflections of kaolinite were observed. The minerals present in the soil of pristine areas can be altered when different uses/managements are adopted. The X-ray diffraction appears to be effective in the evaluation of mineralogical alteration in soils.

PT.14

Gaseous mercury in soils over deeply buried sulphide deposits

Barros FCD[1], Enzweiler J[1], Licht OAB[2], Castilhos ZC[3], Araujo PC[3]
[1]UNICAMP - Instituto de Geociências, [2]MINEROPAR, [3]CETEM – LEMA

The use of gas geochemistry in mineral prospecting of deep ore deposits covered by non-mineralized rocks is described by many authors and the release of gaseous Hg is favored due to the physicochemical properties of this element. The temperature of the formation of the mineralization is a determinant factor for the presence of certain trace elements, including Hg, in many sulfide deposits. Hg has predilection for low temperature zinc deposits, like epithermal and stratabounds deposits. Many mineral deposits also show a strong positive correlation between the Hg content and the amount of sphalerite. The Zn-Pb sulphide deposit of Santa Maria, located in Camaquã Basin, at Rio Grande do Sul, Brazil, was chosen as pilot area for testing emanometry because of the Hg association with the mineralization. During the characterization of the ore deposit, analyses showed up to 7 mg/kg Hg associated to sphalerite. The main objective of this research was to evaluate the potential of using *in situ* measurement of gaseous Hg trapped in the soils as a tool to be applied in the prospecting of Zn-Pb sulphide ore deposits. Gaseous Hg gas was collected from freshly excavated holes at depths of 30 cm and 50 cm, at pre-selected sampling locations 50 m apart and along three transects, two of them over the known ore body. The Hg gas in soil pore was measured during 30 s, after inserting the hose of a portable Hg analyser and the pumping of the air of the hole to into the spectrometer. The concentrations of Hg gas in soil pore were typically low, about 6 ng/L, but significantly higher values, up to 22 ng/L, were observed in specific places. The higher Hg concentrations marked the position of the ore body.

PT.15

Determination of S, Cl, Br and I in natural water by single collector inductively coupled plasma mass spectrometry

Rejas M[1], Gil RA[2], Martinez LD[3], Saavedra J[4], Fernandez Turiel JL[1]
[1]CSIC - INSTITUTE OF EARTH SCIENCES JAUME ALMERA (ICTJA), [2]Universidad Nacional de San Luis. San Luis, Argentine - Instituto de Quimica de San Luis (CCT-San Luis, Area de Quimica Analitica, Facultad de Quimica, Bioquimica y Farmacia, [3]Universidad Nacional de San Luis. San Luis, Argentine - Instituto de Quimica de San Luis (CCT-San Luis), Area de Quimica Analitica, Facultad de Quimica, Bioquimica y Farmacia, [4]IRNASA-CSIC - Salamanca, Spain

The present work describes an analytical procedure for the determination of S, Cl, Br and I in river waters by single collector inductively coupled plasma-mass spectrometry. This study evaluated the effect of instrumental parameters. Ar flow rate, RF Power and Sample flow rate were studied in order to minimize the contribution of polyatomic species to the background. This enabled establishing the resolution required. In order to assess the effect of the sample matrix, the sample composition and preparation (total dissolved solids, organic compounds and acid addition) were also evaluated. The isotopes ^{32}S, ^{34}S, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br and ^{126}I were studied and the contribution of polyatomic ions were mitigated through a careful optimization of the instrumental conditions. Low, medium or high resolutions were compared in terms of background level and sensitivity. After the optimization studies, a robustness test was carried out by means of a Placket-Burman design. The results of this study were compared with those obtained after adding Te and In as internal standards. In that way, their use was suggested when suppress potential bias in the results. The accuracy was assessed by analyzing the reference water sample ICUS-1596, with less than 50 ppm TOC, and with reference values for Cl^- (100.0 ± 0.5 μg ml^{-1}), Br^- (0.2500 ± 0.0013 μg ml^{-1}) and SO_4^{2-} (50.00 ± 0.5 μg ml^{-1}). Since I^- was not informed in those samples, it was determined in spiked samples with increasing amounts of this analyte. The proposed method was applied to actual samples from the Ter and Llobregat rivers, and tap water from Barcelona, Spain. This study was funded by the Project QUECA of the Spanish Ministry of Economy and Competitiveness (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).

PT.16

Low-angle powder x-ray diffraction analysis of mesoporous materials: Comparison between reflection and transmission optics

PAZ SPA[1], ANGELICA RS[2], GOBBO LA[3]
[1]Universidade Federal do Pará - Faculdade de Engenharia de Materiais, [2]UNIVERSIDADE FEDERAL DO PARA - INSTITUTO DE GEOCIENCIAS, [3]Panalytical

Zeolite molecular sieves and other mesoporous materials have been intensively studied due to their potential use in several industrial processes, mainly in catalysis and adsorption. They are characterized by highly ordered hexagonal arrays of unidimensional pores (amorphous walls) with a very narrow pore size distribution ranging from 15 to 100 Å. Structural characterization is mainly carried out by powder X-ray diffraction (PXRD) analysis. The main problem for such analysis is the very low starting angle in order to reach very high d_{hkl} values. Common X-ray diffractometers must be well-aligned and set with very small divergent slits, besides other conditions, in order to get the very low angle peaks. The main purpose of this work is to compare PXRD analysis of such materials carried out both in traditional Bragg-Brentano reflectometry optics and with transmission optics, that have been used more frequently in new laboratory equipments. PXRD equipments used are equipped with Position-Sensitive Detector (PSD), which increases the speed of data collection. For transmission mode, a focusing mirror must be used in the primary beam. MCM-41 is one of the most common mesoporous materials and relatively easy to characterize because the first main peak occurs at 2.2° 2θ (d_{100} ~40 Å, CuKα). On the other hand, the main peak of SBA-15 mesoporous material occurs bellow 1° 2θ (d_{100} ~ 100 Å). For reflection mode, the following conditions must be set: scan range 0.3 to 8° 2θ, 0.02° step size, 60 s time/step, divergent slit of 1/32° and anti scattering of 1/16°. A very important condition set is to reduce the PSD active length from 2.2° to 0.518º. Sample preparations for reflection mode are back-loading sample holders or Si zero background substrate (small amount). For transmission mode, the powder is pressed between kapton films tight with a plastic ring. Results from both analyses are very close with the main advantage in the transmission mode to avoid any care about the starting angle, as primary beam can reach direct the detector. On the other hand reflection mode can is still more frequent in most laboratory equipments, much cheaper but difficult do set the parameters.

PT.17

DEVELOPMENT OF ZrO_2–TiO_2 POROUS CERAMICS SENSING ELEMENTS FOR APPLICATION IN SOILS WATER CONTENT MONITORING

Oliveira, R. M.[1] e Nono, M. C. A.[1]
[1]Grupo de Pesquisa em Tecnologias Ambientais – TECAMB
Laboratório Associado de Sensores e Materiais – LAS
Instituto Nacional de Pesquisas e Materiais – INPE, São José dos Campos, SP - Brasil
Avenida dos Astronautas, 1758, Caixa Postal: 515 - 12.1201 - 970
E-mail: rodmatos@las.inpe.br

The hasty evolution in the area of automation and control of environmental parameters concerning to air and soil moisture monitoring has demanded more and more efforts on the study and improvement of new materials to be applied as sensors and sensing systems more reliable, versatile and at lower cost. The sole chemical and physical properties of the metallic oxides type ceramic materials, allied to their capacity of water molecules surface adsorption, make them excellent candidates for this application. The proposal of this work was an investigation of a porous ceramic sensing element, formerly studied as air humidity sensor, to be applied as moisture sensor in soils water content monitoring. The project aimed the soil water content monitoring in hill landslide hazard areas, which has caused catastrophes in several Brazilian cities, mainly in the last two decades. Therefore, in this work, the porous ceramics manufactured from commercial ZrO_2 and TiO_2 powders, were compacted by uniaxial pressing and sintered at the temperatures 1000, 1100 and 1200 °C. The crystal phases present were identified by X-ray diffractometry (XRD); the analysis of the morphological characteristics and of the microstructures of both the powders and the sintered ceramics were carried out through scanning electron microscopy (SEM). Furthermore, the behavior of the pores sizes distribution curves was obtained by Hg porosimetry. The electric characterization, as function of increasing humidity content of two soil samples, previously selected and characterized, was induced through capacitance measurements. The analyses of the results evidenced that the ZrO_2-TiO_2 porous ceramics sensing elements, developed in this work, are very promising in respect to their potential for utilization as soil moisture content monitoring.

Keywords: porous ceramic; soils water content; sensor elements; hazard areas

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PT.18

Theory of Sampling (TOS) vs. Measurement Uncertainty (MU)

Claas Wagner
ACABS Research Group, Aalborg University, Denmark
Kim H. Esbensen
National Geological Survey of Denmark and Greenland, ACABS Research Group, Aalborg University Denmark

Current measurement uncertainty approaches (MU) are assessed with respect to the complete ensemble of sources affecting the measurement process, in particular the extent to which sampling errors as set forward in the Theory of Sampling (TOS) are appropriately considered in the guides GUM and EURACHEM. All sampling steps, from primary sampling extraction, via laboratory handling, mass reduction and sample preparation procedures to analytical sample size extraction play important roles in the total uncertainty budget, which critically affects the validity of measurement uncertainty estimates. The primary sampling stage is of overwhelming importance. The so-called incorrect sampling errors (TOS) cause a sampling bias that per force will result in varying and unnecessarily inflated MU estimates. The sampling bias cannot be estimated however, as it is inconstant, and can consequently not be counteracted by a conventional statistical bias-correction. TOS stipulates that the sampling bias must be eliminated ("sampling correctness") for which TOS describes appropriate countermeasures. TOS constitutes the only complete scientific theory for representative sampling, enabling appropriate treatment (elimination and minimization) of all MU sources related to sampling. While MU estimates the total measurement uncertainty, it is in reality passive and incomplete without TOS' active sampling correctness paradigm. It is manifestly not enough to regard the incorrect sampling errors as mere "gross errors" which are then conveniently kept out of the MU paradigm. We argue for a reconciliation of the often strongly felt worldview differences between MU and TOS, by proposing to induct TOS fully in MU.

PT.19

Flow injection – array detector ICP-MS: high speed analysis for geochemical mapping

Louise Ander, Simon Chenery, Jennifer Cook and Michael Watts
British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

The new Spectro array detector magnetic sector ICP-MS instrument provides truly simultaneous measurement of isotopes of elements from lithium to uranium. This makes it, potentially, ideal for the measurement of transient signals associated with sample introduction via chromatography, laser ablation or flow injection. In the current study, a ASXpress™ flow injection device was coupled to the Spectro ICP-MS instrument to minimise uptake, analysis and washout times.

One of the parameters initially assessed was the influence of signal acquisition times of between 1 and 60 seconds on detection limits and repeatability.

Groundwaters were then analysed using a 2-minute programme on the Spectro instrument and the data compared with those acquired with a 8-minute analytical programme on a conventional Agilent 7500 series quadrupole ICP-MS instrument. In general there was good agreement, within experimental error, between the two sets of data for many major and trace elements. However, for certain elements, such as As and Se, it was concluded that collision cell technology is required to obtain accurate data.

Finally, we present an evaluation of the measurement of iodine in soils from a European-wide survey. Iodine is often considered to be a difficult element to determine by ICP because of memory effects caused by inconsistent wash-out between samples. Because the sample preparation involved extraction with tetramethyl ammonium hydroxide (TMAH), a different set of analytical conditions from the routine programme was required. The flow injection system maximised the number of samples that could be analysed in a single session whilst minimising the concentration of the TMAH reagent necessary for wash-out, resulting in significant cost savings.

PT.20

IMS 1280-HR: a versatile SIMS instrument for Geosciences

Houssou A[1], Peres P[1], Fernandes F[1], Schuhmacher M[1]
[1]CAMECA

SIMS (Secondary Ion Mass Spectrometry) is applied to a variety of applications in Geosciences, because it provides *in situ* measurement of elemental and isotopic composition in selected µm-size areas of the sample.

The CAMECA IMS 1280-HR large geometry SIMS offers outstanding capabilities for a wide range of geological applications, thanks to its very high transmission mass spectrometer combined to a versatile multicollection system. The IMS 1280-HR is also able to map the lateral distribution of major, minor, and trace elements.

Hundreds of scientific papers have been published covering major application fields in geo- and cosmochemistry, geochronology, environmental studies,...:

- stable isotope ratio measurements on different systems: H [1], Li [2], C [3-5], O [6-10], Mg [11], Si [12], S [13-14],...
- U-Pb dating in Zircon [10,15-18],
- trace element analyses [10, 19-20],

A review of recent analytical data obtained with the IMS 1280-HR on different domains will be presented.

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PT.21

A trace-element study of tourmalines from the Passagem de Mariana gold mine tourmalinites (Minas Gerais, Brazil) by LA-ICPMS

Garda GM[1], Andrade S[2]
[1]Instituto de Geociências da USP - Departamento de Mineralogia e Geotectônica, [2]Instituto de Geociências da USP - Laboratório de Química e ICP

A trace-element study was carried out in three types of tourmaline from tourmalinites of the Passagem de Mariana Gold Mine (Minas Gerais, Brazil). *In-situ* analyses were performed in the IGc-USP Laboratory of Chemistry and ICP, equipped with a New Wave UP-213 laser ablation system coupled to an Elan 6100DRC ICP-MS. Ultrasound cleaned, 80 mm-thick polished tourmalinite sections were analyzed. Diameter crater varied from 40 to 65 mm when in spot mode and from 30 to 40 mm at a 2 mm/s speed when in raster mode. Average time of analysis was 120 s. Reference materials used for calibration were synthetic glasses BHVO-2G, BCR-2G (USGS) and SRM-612 (NIST). The results were treated during each analysis by means of the Glitter 4.4.2 software for instrumental drift and fractionation corrections adopting NIST SRM-612 as internal standard. MgO contents obtained by EPMA were used to adjust each analysis.

Type-1 tourmaline is very fine-grained and composes massive tourmalinites occurring as continuous or boudinaged bodies and as fragments in quartz-carbonate veins and breccias. Type-2 tourmaline is fine-grained, color-zoned and constitutes massive and banded tourmalinites. Type-3 tourmaline is coarser-grained and color-zoned, grown with long axis perpendicular to the contact of tourmalinite fragments with quartz-carbonate matrix in veins and breccias (comb texture). The three types of tourmaline are Mg-rich (Mg# from 0.64 to 0.73). EPMA analyses suggest sector zoning, characterized by decreasing SiO_2 and Al_2O_3 and increasing MgO, Na_2O, F and in particular CaO with increasing TiO_2 contents. In type-2 tourmaline, it corresponds to color zoning, once greenish zones yield TiO_2 <0.5 wt.% and brownish zones yield TiO_2 >0.5 wt.%.

Trace-element variations attest for sector zoning in type-1 and type-2 tourmalines, with increase in Sr, Ni, V, Pb, Y and REE contents with increasing Ti. In contrast, trace-element variations in type-3 tourmalines follow a different pattern, with very low, almost constant Co, Ni, Hf, Zr, Y and REE contents and low Sr and Pb and high V contents, which increase as Ti increases. When compared to type-1 and type-2 tourmalines these variations indicate charges in the host environment, probably caused by gold-mineralizing fluids associated with veining and brecciation.

PT.22

Study of carbonates and related reservoirs by 3D x-ray microtomography

I.Lima(1) and R.T.Lopes(1)
(1) Nuclear Instrumentation Laboratory, PEN/COPPE-UFRJ, RJ-Brazil
PoBox: 68509, ZIP: 21941-972

There are many applications in the oil and gas area, such as the characterization of its microstructures. One the main parameter is the porosity. Carbonates and sandstones can store oil and gas because it's both porous and permeable. Porous can mean that liquid and gas can be held and stored and permeable means that liquids can flow through. Acid injection on carbonate rocks, for example, has the purpose to create wormholes through which oil and gas will flow after reservoir stimulation. In this context, it is worthwhile to conduct laboratory investigations of the response of cores to different porous medium and acid injection conditions. 3D X-ray microtomography is a non destructive imaging technique which is able to examine rocks internal structure with micron resolution. The technique works by passing X-rays towards an opposed detector which records the intensities of the X-rays transmitted through an object which is being rotated perpendicular to its axis. The detector records a series of radiographs images spaced of a certain angle and they are later reconstructed in order to produce 3D internal image of the object. The goal of this work is to apply this technique in the study of carbonate reservoir cores porous media in several experimental conditions with high spatial resolutions. From the results it is possible to characterize the micro-porosity architecture and have a better understanding of this media.

PT.23

Elemental Spatial Distribution in Horse Mussel *Modiolus modiolus* Shells by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

D. Asogan[1], M. Beisheim[1], S. R. N. Chenery[2]
[1] *CETAC Technologies, 14306 Industrial Road, Omaha, NE 68144, USA*
[2] *British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK*

The bivalve *Modiolus modiolus* (Horse Mussel) shell exhibits incremental growth bands that incorporate elements in the surrounding medium in which it grows. Mapping the elemental distribution of these growth bands can yield information relating to a number of different factors such as seasonal temperature variation or geolocation.

Laser Ablation ICP-MS is a microanalysis technique that can accurately introduce solid samples for nuclide identification and provide information on their spatial distribution within samples. Applied to the growth bands discussed above, it is possible to visualize the elemental distribution and, therefore, seasonal variations of elements during the growth period of the shell.

This paper shows the technical feasibility of LA-ICP-MS as a technique for visualizing the spatial distribution of elements within the mussel shell using a CETAC LSX-213 G2 laser ablation system.

PT.24

U-Pb analysis procedures using LA-ICP-MC-MS in magmatic zircons of the Santa Clara Rapakivi Massif in the SW Amazonian Craton

Nogueira CC[1], Geraldes MC[2]
[1]Universidade do Estado do Rio de Janeiro - Programa de Pós-Graduação em Análise de Bacias e Faixas Móveis - Faculdade de Geologia, [2]Universidade do Estado do Rio de Janeiro - Departamento de Geologia Regional e Geotectônica - Faculdade de Geologia

The LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry) is a widely used technique especially due to its simple procedure and the possibility of analyzing the isotopic compositions in individual grains and in specific areas of zircon grains. This technique also dispenses sample cleaning and the necessity of an extremely clean laboratory environment.

In this work, we used the LA-ICP-MS technique to determine U-Pb ages of two samples of granites collected from the Santa Clara massif, in Cujubim, Rondônia.

The analyses were performed using a ThermoFisher Neptune multi-collector ICP-MS coupled with a laser ablation system Nd-YAG 213nm. The laser ablation spots sizes used in this work were 35 µm in diameter; the frequency used was 10 Hz and the energy was 78% in one sample (SC-14A) and 82% for the other sample (SC-30A). Static fractionation, including those caused during laser ablation and due to instrumental discrimination, was corrected using a external zircon standard called "GJ".

The zircon grains were selected using a binocular microscope and are colorless, faceted prisms and do not show major igneous zoning. However, the grains are characterized by micro-fractures and apatite inclusions. No signs of abrasion were observed as well.

The results show that most part of the zircons are concordant (<10% of discordance) and exhibit Th/U ratios ranging from 0.3 to 0.6, values associated with zircons derived from acid to intermediate magmatic rocks. A total of six grains was used in order to create an isochron and the points defined ages of 1075±16 Ma for the sample SC-30A, (hornblende-biotite granite porphyritic). A total of seven grains was used from the sample SC-14G (fine-grained biotite granite) to generate an isochron and the points defined ages of 1061±11 Ma. These results suggest that the fine-grained facies of the Santa Clara Rapakivi Massif was emplaced approximately 15 Ma after the porphyritic facies. These results are in accordance to the features observed and described during the mapping of this batholith.

PT.25

THE APPLICATION OF U-Pb GEOCHRONOLOGY TO TITANITE BY LASER ABLATION ICP-MS

Kei Sato, Miguel A. S. Basei, Walter M. Sproesser, Oswaldo Siga Jr
Instituto de Geociências da Universidade de São Paulo, Rua do Lago 562, Cidade Universitária,
São Paulo - Brazil - CEP05508-080 - e.mail: keisato@usp.br

Key words: titanite, LA-ICP-MS, Khan, Namibia

Several large titanite crystals were collected from Khan copper mine, Namibia - Africa with intention of establishing a reference in the ^{206}Pb/^{238}U ratio to normalize titanite unknown. Previous analysis from three distinct authors shown the following results: ^{207}Pb/^{206}Pb age of 518± 2 Ma and 522.3 ± 2.3 Ma by TIMS and concordia age of 516.9Ma by LA-ICP-MS.

Isotopic data were acquired using a NEPTUNE – ICP-MS coupled by an excimer laser ablation system. The cup configurations utilized to U-Pb data acquisition were IC_3 = ^{202}Hg, IC_4 =^{204}(Hg+Pb), L_4 = ^{206}Pb, IC_6 = ^{207}Pb, L_3 = ^{208}Pb, H_2 = ^{232}Th and H_4 = ^{238}U where L and H were low and high mass to faraday cup position and ICs are ion counting (continuous dynode system). The ICP configurations were: Radio Frequency power = 1100W, cool gas flow rate = 15L/min (Ar), auxiliary gas flow rate = 0.7L/min (Ar), sample gas flow rate = 0.6L/min. Laser Setup: energy = 6mJ, repetition rate = 5 Hz, spot size = 38 µm, helium carrier gas`= 0.65L/min. The routine U-Pb analysis consists of 2 blanks, 2 NIST, 3 external standard, 13 unknown grains, 2 external standards and 2 blanks measurement. Each run consist of 40 cycles with 1 second per cycle. The ^{204}Hg interference on ^{204}Pb was corrected by ^{202}Hg where the value of ^{204}Hg/^{202}Hg ratio is 4.2. To ^{207}Pb/^{206} ratio normalization a combination of NIST and external standards was used and the normalization of ^{206}Pb/^{238}U ratio an external titanite standard was used.

Khan titanite typically contains significant quantities of common Pb, therefore the accuracy of ^{207}Pb/^{206}Pb and ^{206}Pb/^{238}U ratios obtained is critically dependent on the correct assessment of the common Pb component. For this paper, the residual common Pb was corrected based on ^{204}Pb measurement using terrestrial composition (Stacey Kramer). The range of total common Pb on Khan titanite is among 1 and 8 ppm. The total radiogenic Pb is between 27 and 44 ppm, the ^{232}Th/^{238}U ratio ranged from 0.5 to 1.8 and U concentration varied among 220 and 460 ppm.

The concordia diagram from 4 Khan titanite fragments, using external standard of the same titanite (520Ma), show a age of 528 ± 6Ma. The MSWD value of 3.8 is too high indicating low homogeneity for the analyzed fragments.

PT.26

High sensitivity laser ablation MC-ICP-MS

Nicholas S. Lloyd[1]*, Steve Shuttleworth[2], Claudia Bouman[1], Anne Trinquier[1], John Roy[2] and Johannes B. Schwieters[1]
[1]Thermo Fisher Scientific, Bremen, German, nicholas.lloyd@thermofisher.com (* presenting author)
[2]Photon Machines, Redmond, USA, shutts@photon-machines.com

The Thermo Scientific NEPTUNE *Plus* MC-ICP-MS with Jet Interface option has previously been demonstrated to offer the highest ICP-MS sensitivities for desolvated solutions [1] and for laser ablation. A combination of nitrogen addition, special cones and a high capacity interface pump improved laser ablation Hf sensitivity by a factor of more than seven. The resulting sensitivity enabled highly precise and accurate ^{176}Hf/^{177}Hf isotope ratios to be measured from 25 µm diameter laser ablation spots, whereas typically this level of accuracy and precision could only be achieved with 50 µm diameter spots (with four times the ablated volume). It was noted that with increased sensitivity the Yb and Hf fractionation factors diverge further, highlighting the importance of independent measurement of the Yb fractionation factor for the ^{176}Yb correction.

For these experiments a Photon Machines Analyte. G2 193 nm laser ablation system was operated with moderate fluence and repetition rate (6.22 J/cm^2 at 7 Hz). The short pulse width and short wavelength of this excimer laser system is ideal for ablation of zircon mineral grains. The Analyte.G2 is equipped with a two volume HELEX 2 cell for the fastest washout time. The combination of improved ICP-MS sensitivity and fast response laser ablation cell is critical for obtaining spatially resolved isotope ratio data.

In this poster we describe a new multi-ion counting collector configuration that has been designed for the NEPTUNE *Plus*. This allows for increased flexibility of analysis, using combinations of ion counters and Faraday cups to accommodate the range of U-Pb isotope beam intensities expected from both young and old zircons. We further investigate the factors that influence external precision of ^{176}Hf/^{177}Hf isotope ratios from zircons, including the effects of nitrogen addition on analyte sensitivity and mass bias stability.

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PT.27

Investigation of the concentrations and mixing behaviour of transition elements from subgroups IV, V and VI (Ti,Zr, V and Mo) in the Elbe, Rhine and Weser estuaries

Schneider AB[1], Kiprotich J[2], Koschinsky A[2], Pöhle S[2], Schmidt K[2], do Nascimento PC[3]
[1]Universidade Federal de Santa Maria (UFSM) e Jacobs University Bremen (JUB) - Departamento de Química (UFSM) / Earth and Space Sciences (JUB), [2]Jacobs University Bremen - Earth and Space Sciences, [3]Universidade Federal de Santa Maria - Departamento de Química

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Trace elements are transported by river systems in dissolved, colloidal and particulate forms. The change in the gradients of parameters such as ionic strength, pH, and redox conditions during estuarine mixing results in a range of physico-chemical processes which modifies the trace element distribution over the three phases considerably. This is largely due to the mobilization, flocculation and sedimentation processes, and also the resuspension of bottom sediments. In the present study we have carried out experiments with the aim of gaining more insight in the behaviour of both dissolved and particulate trace metals Ti, Zr, V and Mo during mixing in the Rhine, Elbe and Weser estuaries. The river water and seawater were mixed in different ratios, i.e. 100:0, 90:10, 80:20, 70:30 and so on. Two mixing setup procedures were carried out; firstly, 0.2 µm filtered river was mixed with unfiltered seawater and the mixture allowed to equilibrate for 24 hrs and then filtered using a 0.2 µm filter. A second mixing series was made by mixing unfiltered river and seawater and the mixture filtered with 0.2 µm filter after 24 hrs of equilibration. UV-irradiation and determination by adsorptive stripping voltammetry were used for the analytical determination. Our preliminary mixing experiments have yielded interesting results that had not been previously reported. The enrichment of both Ti and Zr at 50:50 river : seawater mixtures will especially be a subject of further investigation in other experiments. Both Ti and Zr show a non-conservative mixing behaviour with similar surface distributions because of their similar chemistry during the mixing. Ti and Zr are strongly particle reactive elements, hence are rapidly removed from solution at low salinities during mixing in the rivers. The concentrations of both Mo and V are highest in seawater suggesting that there is very little estuarine removal of these elements. Mixing curves indicate that adsorption/desorption has only a small effect in regulating the concentrations of Mo and V compared to Ti and Zr.

PT.28

Distribution of zirconium, hafnium, niobium and tantalum in marine ferromanganese crusts

Schmidt K[1], Koschinsky A[1], Bau M[1]
[1]Jacobs University Bremen - Earth and Space Sciences

Hydrogenetic ferromanganese crusts precipitate from seawater. Very slow growth rates and the high adsorption capacity for dissolved elements lead to the accumulation of large quantities of metals from seawater and make them generally suitable for the investigation of environmental and paleooceanographic conditions in the past. The crusts are used as archives of paleo-seawater isotopic and elemental composition and the record of radiogenic isotope ratios (e.g., Hf) is widely applied.

Here, we represent new concentration data for the high field strength elements Zr, Hf, Nb, and Ta from crust surfaces and bulk samples from the NE Atlantic and the Central Pacific obtained wit ICP-MS. Accuracy and precision of chemical analyses were assured with the certified reference materials JMn-1, Nod-P-1, GSPN-3, and GSMC-1. We report the first Ta data for GSPN-3 and GSMC-1.

Concentrations of Zr, Hf, Nb in surface samples and bulk samples of hydrogenetic ferromanganese crusts are strongly enriched (Zr, Hf, Nb) relative to bulk continental crust concentrations, while Ta is moderately enriched. Detrital contribution is only minor and the hydrogenetic enrichment from seawater is proven. In deep seawater, Zr-Hf is strongly fractionated and distinctive for individual water masses, while Nb/Ta is rather uniform and close to the chondritic ratio (Firdaus et al., 2011). Neither the crust surfaces nor the bulk samples of Fe-Mn crusts display the total dissolved Zr/Hf or Nb/Ta ratios of modern deep seawater. This implies that the geochemical twin elements are fractionated during incorporation into oxide deposits, which makes them unsuitable as proxy tracer for changes in paleocirculation as previously suggested by Frank et al (2011). Further, concentration and fractionation of the both element pairs depend on accumulation time. Ferromanganese crusts recovered in the NE Atlantic and Central Pacific Ocean are characterized by systematic differences in their HFSE distribution: bulk crusts from the Atlantic Ocean are relatively more enriched in Hf and Ta relative to Zr and Nb, respectively, which is likely related to the respective seawater signatures.

Firdaus et al, 2011: Nature Geoscience 4, 227–230
Frank, M., 2011: Nature Geoscience 4, 220–221

PT.29

Model of spatial distribution of ^{40}K and ^{137}Cs in marine sediments of the southeastern Brazilian upper margin

Ribeiro AP[1,2], Figueiredo AMG[1], Figueira RCL[3], Osman JO[4], Wasserman JC[5]
[1]Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, Brazil, [2]Universidade Nove de Julho, Diretoria da Saúde, Rua Vergueiro, 235, 01505-001, São Paulo, Brazil, [3]Instituto Oceanográfico - Universidade de São Paulo, Pça. do Oceanográfico, 191, 05508-900, São Paulo, Brazil, [4]Centro Federal de Educação Tecnológica de Sergipe, Av. Eng. Gentil Tavares da Motta, 1166, 49.05260, Aracaju, Brazil, [5]Rede de Meio Ambiente e Desenvolvimento Sustentável-Universidade Federal Fluminense, Rua Outeiro de São Batista, s/n, 24020-149, Niteroi, Brazil

There is a lack of knowledge regarding the distribution of radionuclides in superficial marine sediments of the southeastern Brazilian upper margin. Through the means of high-resolution gamma ray spectrometry, ^{40}K and ^{137}Cs radioactivities were quantified in over 90 sediment samples between 50 and 1,000 m isobaths for the construction of a model of spatial distribution in marine sediments. The activities obtained are 49.28 – 589.10 Bq kg^{-1} for ^{40}K and 0.27 – 3.31 Bq kg^{-1} for ^{137}Cs. Also, it was seen that this radionuclides distributions have a latitudinal differentiation, probably due to the different physical and sedimentary processes dominant in each sector of the study area.

PT.30

Acid volatile sulphide (AVS) and simultaneously extracted metals (SEM) procedure compared to attenuation model to assess heavy metal mobility in sediments from Sepetiba Bay, Rio de Janeiro, Brazil

Ribeiro AP[1,2], Figueiredo AMG[1], Figueira RCL[3], Osman JO[4], Wasserman JC[5]
[1]Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, Brazil, [2]Universidade Nove de Julho, Diretoria da Saúde, Rua Vergueiro, 235, 01505-001, São Paulo, Brazil, [3]Instituto Oceanográfico - Universidade de São Paulo, Pça. do Oceanográfico, 191, 05508-900, São Paulo, Brazil, [4]Centro Federal de Educação Tecnológica de Sergipe, Av. Eng. Gentil Tavares da Motta, 1166, 49.05260, Aracaju, Brazil, [5]Rede de Meio Ambiente e Desenvolvimento Sustentável-Universidade Federal Fluminense, Rua Outeiro de São Batista, s/n, 24020-149, Niteroi, Brazil

Sepetiba bay, located about 60 km west of the metropolitan region of Rio de Janeiro city, has undergone notable development in the last decades, with the establishment of industrial plants in its basin, which release its industrial waste either straight into the bay or through local rivers. The Sepetiba harbor also brought up a lot of industrial investment in that area. This urban and industrial expansion caused several environmental impacts, mainly due to the presence of heavy metals and other potentially toxic substances present in the effluents sent out into the bay. This work aimed to assess heavy metal (Cd, Cu, Ni, Pb e Zn) contamination in Sepetiba bay. The Σ[SEM]/[AVS] model were applied in 65 sediment samples from Sepetiba bay, representing the whole area. The results obtained showed that Cd, Cu, Pb and Zn presented higher concentrations in the northeastern area (mainly in the mouth of Guandu and Canal de São Francisco rivers), while the highest concentration of Ni were observed in the western region of the bay. The relation Σ[SEM]/[AVS] was below 1 in the northeastern region, indicating that, in spite of the high concentration of the analyzed metals in this area, they are trapped in the sediment, as sulfides. The total metal concentrations in the sediments were also determined and the same distribution patterns obtained for the SEM were observed, with high concentrations in the northeastern region of the bay. Further, a geostatiscal approach is presented, the attenuation of concentrations model, which aims to estimate metal mobility in sediments. The proposed model showed the highest attenuation values for Zn, Cd, Cu and Pb in the northeastern region, indicating that the mobility of these metals is low in this region, suggesting low availability, which is in good agreement with the results obtained by the Σ[SEM]/[AVS] model. These results indicate good possibilities of applying this model in metal contamination studies in estuarine ecosystems.

PT.31

A new method of Mg purification and Mg isotope analysis

J.-S. Ryu[1], M.S. Choi[1], S.-W. Lee[1], H.S. Shin[1], K.-S. Lee[1]
[1]Korea Basic Science Institute - Division of Earth and Enviromental Sciences

Magnesium isotopes, one of important elements in lithosphere and biosphere, allow to directly tracing the Mg cycles. Many studies have presented the separation schemes of Mg and Mg isotope compositions in various sample types. Here, we present newly developed Mg separation method and verify it providing Mg isotope compositions (expressed as δ^{26}Mg relative to DSM-3) of various rock standards. All matrix cations causing significant mass bias were effectively removed through newly developed Mg purification steps, where the Mg yield was over 95% and the matrix concentration did not exceed 5% of the Mg concentration. Mg isotope ratios were measured using a Neptune MC-ICP-MS equipped with X-cone under cool-plasma condition. The long-term reproducibility of CAM-1 yielded −2.609 ± 0.078‰ of $\delta^{26}\mathrm{Mg}_{\mathrm{DSM\text{-}3}}$ (2σ, n=16). Mg isotopic compositions in various international rock standards having wide ranges of major element compositions ranged from −0.043 to −0.430‰, in good agreement with reported values (Huang et al., 2009 and references therein). This study suggests that newly developed Mg purification method and modified analytical technique here are very efficient and competitive.

PT.32

Low Dilution Glass Bead Digestion Method for the Trace Element Analysis of Rock Samples

Park C.-S.[1], Shin H.S.[1], Cheong C.-S.[1], Oh H.[1], Moon J.H.[2], Cho H.[1]
[1]Korea Basic Science Institute - Division of Earth and Environmental Science, [2]Korea Atomic Energy Research Institute - Neutron Science Division

In inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS), open beaker digestion method is routinely used as a sample preparation method for trace element determination of rock samples. With this method, however, dissolution of Zr and Hf is not always guaranteed especially for analyzing samples including refractory minerals. In this study, we have compared the results from the glass bead digestion method with conventional open beaker digestion method using four USGS reference materials (AGV-2, BHVO-2, G-3, GSP-2). Thirty trace and rare earth elements were analyzed by ICP-AES and ICP-MS. The results show no clear differences for the AGV-2 and BHVO-2. But Zr, Hf and Y concentrations of the G-3 and GSP-2 were significantly lower than the recommended values in case of open beaker digestion method. On the contrary, all the analytical results of the G-3 and GSP-2 using glass bead digestion method were in good agreement with the recommended values, indicating complete dissolution of refractory minerals (e.g. zircon). The analytical results show that the volatile elements such as Pb and Zn were not lost during the preparation of glass beads. Results indicate that low dilution glass bead digestion method is helpful to enhance precision and accuracy of trace element analysis for geological samples with refractory minerals.

PT.33

Precise determination of lithium isotope ratio in geological sample by MC-ICP-MS with cold plasma.

SHIN HS[1], Choi MS[1]
[1]Korea Basic Science Institute

Lithium has two naturally occurring isotopes – ^{6}Li and ^{7}Li - with relative abundances of 7.5 % and 92.5 %, respectively. Lithium isotope has the potential to reveal important information concerning a wide range of nuclear technology, biomedicine, astrophysics, and geochemistry. , Li isotope studies have largely focused on the search for the analysis of geological materials with variable degrees of accuracy by thermal ionization mass spectrometry (TIMS) technique. With the advent of multi-collector inductively coupled mass spectrometry (MC-ICP-MS), however, it is now possible to routinely measure Li isotopes with greatly improved precision compared to traditional techniques such as thermal ionization mass spectrometry. However, this technique has been interrupted by baseline interference (isobaric interference) mainly on mass 6 and 7 during ionization. The analytical difficulty is mainly caused by the primarily reflect scattered hydrogen ions, double charged nitrogen and carbon ions at higher RF power. , we improved the baseline interference in Ar plasma based on cold plasma (700 W) technique. The rock samples were digested by mixed acid (HNO_3, HF, $HClO_4$) and separated by ion exchange resin and the seawater samples were separated by cation exchange resin (BioRad AG 50W-X8 200-400 mesh). The data were collected by bracket method (standard-sample-standard) for the correction of isotope variations , L-SVEC (NIST L-SVEC Li_2CO_3) was used as a standard.

PT.34

A preliminary study on speciation of rare earth elements in pore water in sedimentary rock formation

M Fukai[1], Y Kikawada[2], T Oi[2]
[1]Sophia University - Graduate School of Science and Technology, [2]Sophia University - Faculty of Science and Technology

The behaviour of rare earth elements (REEs) is a useful means to understand subsurface water-rock interactions in connection with high-level radioactive waste management. Their behaviours in subsurface environments are, however, complicated because they can exist in various chemical forms in fluids and be diversely distributed between solution and solid phases. It is important to know speciation of REEs and their concentrations in natural waters.

We developed a new REEs speciation technique in aqueous solutions using a chelating resin having imminodiacetate groups (Chelex 100, Bio Rad). With the resin, each REE was fractioned into two groups. The one (inorganic fraction) consists of the free ion and inorganic REE complexes such as carbonates and sulfates, and REE ions interacting with organic substances like humic and fulvic acids may comprise the other (organic fraction).

We conducted leaching experiments where REEs were leached from mudstone with a weakly basic solution (0.05 mol/dm^3 NaCl-$NaHCO_3$). The experiments simulated natural pore water-sedimentary rock interactions. We then applied our speciation technique to leachates of those experiments. The resin was immersed in the leachate and then separated from the solution by filtration. We reasonably assumed REEs in inorganic forms were trapped by the resin (inorganic fraction), while those in organic forms remained in the solution (organic fraction).

The mudstone-normalized REE patterns were different between the inorganic and organic fractions. The former showed the REE pattern having a positive slope, which was similar to that of stability constant of REE carbonates. This suggested that the REE pattern of the inorganic fraction was mainly controlled by complexation of REEs with carbonate and/or bicarbonate ions. The organic fraction has a specific REE pattern with positive Ce anomaly, which may reflect the relative stability of REE complexes with organic substances.

The present speciation technique is helpful to deepen our understanding of natural water-rock interactions.

PT.35

Suppression of fluoride precipitation during acid dissolution of silicate rock samples

Navarro MS[1], Enzweiler J[1]
[1]Universidade Estadual de Campinas - Instituto de Geociências

The determination of trace elements in silicate rock samples by ICP-MS is frequently performed after decomposition of all mineral constituents using HF and HNO_3 at high temperature and pressure conditions. However, such conditions may favour the precipitation of fluorides of Ca, Mg, Na and Al that may remain insoluble at the end of the procedure. The coprecipitation of trace elements results in their incomplete recoveries. The nature and amount of the insoluble precipitate depend on the composition of the sample.

The addition of $HClO_4$ during the evaporation steps efficiently decomposes the fluorides originated during the dissolution of mafic rocks, mainly analogues of ralstonite and MgF_2. But the precipitate formed during the dissolution of felsic rocks, mainly AlF_3, remains insoluble in $HClO_4$. The addition of Mg is used to increase the molar ratio (Mg+Ca)/Al and induce the formation of MgF_2 instead of AlF_3.

Experiments with the dissolution of the reference material BRP-1 (basalt) showed absence of precipitate independently of the mass, not requiring the addition of $HClO_4$. This acid evaporates slowly, is dangerous and introduces interferences during analysis in the ICP-MS.

To avoid the precipitation of fluorides during the digestion of acid rock samples and using $HClO_4$ to decompose them, the efficiency of manipulating the matrix by adding major elements (Mg, Ca, Al and Fe) to match BRP-1 composition was tested.

Test portions of reference materials RGM-1 (rhyolite) and GSR-1 (granite) were treated with four variations of the acid dissolution method (0.1 g sample; 0.5 mL HNO3, 2 mL HF, 5 days, 200 °C, Teflon bomb). They consisted of: (a) adding HClO4 during evaporation, (b) not adding HClO4 during evaporation, (c) reducing the amount of HF and (d) doping the reference material, before the attack, with Fe2O3, MgO and CaO, to reach the same molar ratio of the reference material BRP-1, without adding HClO4 in the evaporation step. The results showed that the manipulation of the matrix (method d) improved the recoveries of many of the twenty seven measured elements (Rb, Sr, Zr, Nb, Cs, Ba, Hf, Ta, Pb, Th, U and rare earth elements) when compared to other tested methods.

PT.36

Cavity ring-down spectroscopy (CRDS) as a tool for the determination of carbon isotopic distribution in biomass and biofuel samples

Martins JMA[1], Godoy JMO[1], Tonietto GB[1], Silva MAD[1], Ribeiro WRS[1]
[1]Pontifícia Universidade Católica do Rio de Janeiro - Departamento de Química

Biomass is a material made of organic substances, that is, animals and plants. Its use is important in the development of new energy alternatives, because through the use of biomasses biofuels can be produced, which are a renewable energy source. Among the biofuels that can be produced from biomass, are ethanol, bio-oil, biodiesel and biogas. It is crucial to discern the characteristics of biomasses and their biofuels. A way of characterizing these materials is through the determination of the carbon isotopic ratio ($^{13}C/^{12}C$). This methodology is extremely useful in the carbon quantification of different botanical species, because it is based on the isotopic fractionation of the carbon associated with photosynthesis. The assimilation of atmospheric CO_2 can be obtained through three distinct forms, but only two forms are most commonly used, throughout the photosynthetic cycle of C3 (Calvin-Benson Cycle) and C4 (Hatch-Slack Cycle) plants. Several techniques are used to perform the determination of natural isotope concentrations and their variations, with isotopic ratio mass spectroscopy (IRMS) being the most widely used. An analytical technique that is gaining market space is the cavity ring-down spectroscopy. Unlike mass spectrometers, these analyzers require little or no sample treatment, thereby reducing the analysis time. The present study aimed to obtain the $^{13}C/^{12}C$ isotopic signature in sugar, biomass (sugarcane bagasse, liginin, capim elefante and sawdust), biofuel (ethanol) and sawdust bio-oil samples using a laser analyzer. An isotopic analysis method using a total organic carbon analyzer coupled to a cavity ring-down spectrometer (iTOC-CRDS) was developed and implemented. The results were compared with those obtained by IRMS. The methodology was validated according to Eurachem and ISO GUM guides.

PT.37

Minor and rare earth elements as paleoenvironmental markers of late Quaternary sediments in Marajo island, Northern Brazil

Rossetti DF[1], Munita CS[2]
[1]Instituto Nacional de Pesquisas Espaciais, INPE, [2]Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP

Estuaries are characterized by high lateral and vertical facies variability that results from complex interaction of fluvial and marine processes. Where only core data are available, the recognition of estuarine deposits in the ancient record is problematic based only on sedimentological studies due to the difficult assessment of both sedimentary processes and body geometry. Exploring proxies that can be used in combination with sedimentary parameters is important for helping reconstructing estuarine paleoenvironments. Geochemical tracers including Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sm, Sc, Ta, Th, U, Yb, and Zn have good potential for paleoenvironmental purposes. However, additional studies are needed in order to further demonstrate the success of these proxies to interpret various depositional environments formed within estuarines. This type of approach was applied to a late Quaternary succession in northern Brazil, where available studies integrating morphological analysis, sedimentary facies and isotope data had led to distinguish among several estuarine depositional environments. Multivariate analysis of trace and REE allowed distinguishing five geochemical groups, which conform to previously reconstructed fluvial, outer estuarine, central estuarine basin, tidal flat and lagoon deposits. In particular, the dendrogram, as well as principal component (PCA) and discriminating (DA) analysis allowed a clear distinction between fluvial influenced (i.e., fluvial and central estuarine basin) and relatively more marine influenced (outer estuarine, central estuarine basin and tidal flat) deposits. The distribution of geochemical tracers in the analysed deposits had a strong influence of variations in salinity and pH that typify these depositional environments, though some of the changes might have also responded to other processes as adsorption due to the influence of colloidal material, mineralogical influence, airborne deposition and burrowing. The results of the present study lead to suggest that trace and rare earth elements might be a useful tool to distinguish depositional environments associated with ancient estuarine systems.

PT.38

Heavy metals concentrations in sediments as influenced by livestock activities in Central Brazil

Rocha C[1], De-Campos A B[2], Gonçalves Jr. A C[3], Tejerina_Garro F L[4], Prado D[4], Moreira A C N[4]
[1]Pontificia Universidade Catolica de Goias - Dep. Matematica e Fisica, [2]Universidade Federal de Goiás - Instituto de Estudos Sócio-Ambientais, [3]Universidade do Oeste do Paraná - Dep. de Química Ambiental, 4Pontifícia Universidade Católica de Goiás - Dep. de Biologia

Heavy metals are among the most common environmental pollutants. They are found in waters, sediments, and biota due to natural or anthropogenic sources, e.g. ore deposits, industrial-urban and agriculture- livestock activities. Livestock activities are growing in Central Brazil however little is known about their effects on heavy metals concentrations in sediments. This study aimed to determine the concentrations of Cu, Zn, Mn, Fe, Cd, Pb, Cr, Al in sediments collected at channels associated to livestock activities. The selected livestock sites belonged to family farmers in which the cattle have access to channels and defecate in or close to water bodies. Thirty-four livestock sites located at the riverbank of tributaries of the Meia Ponte River, Goias State, Brazil, were selected for this study. Bed-load sediment samples were collected in the channels up and downstream from the livestock sites using an Eckman type dredge. Sediments of each site were homogenized and stored into plastic bags at 4 °C until further analysis. Before chemical extraction, the samples were sieved to obtain the grain-size fraction of 0.063mm. Extractions were performed by acid oxidative reaction using HNO_3/H_2O_2 followed by heavy metals determination using atomic absorption spectrometry. The data were treated using test-t to verify differences between metals concentration from up and downstream samples. Average values were high for all metals from both up and downstream samples, remarkably for Al and Zn, and higher than the heavy metal standards specified by the Brazilian legislation for water class 3. The high Al and Fe concentrations may be explained by the soil composition which is naturally rich in these metals. For the other metals, the high concentrations may be related to anthropogenic sources from livestock. An interesting finding of this study is that significant changes in Fe and Zn concentrations were found between up and downstream samples. Surprisingly the Fe and Zn concentrations were higher for upstream samples. We believe that the detected changes are associated to livestock activities mainly sediment disturbance by cattle treading, which may influence metal losses. In conclusion, family farmers' livestock activities close to fluvial channels may not increase bed-load sediment pollution by heavy metals.

PT.39

Chemical fractionation of heavy metals and metalloids in tailings and stream sediments around the Terramonte Ag-Pb–Zn mine, northern Portugal shown by the modified BCR sequential extraction

PAULA C. S. CARVALHO*, ANA M. R. NEIVA, MARIA M. V. G. SILVA
Department of Earth Sciences, Geosciences Centre, University of Coimbra, 3000-272 Coimbra, Portugal
*Presenting author: paulacscarvalho@gmail.com

The old Terramonte mine is located at about 18 km at east of Porto, northern Portugal. The Ag-Pb-Zn quartz veins cut the Cambrian Schist-Metagraywacke Complex, filled N 60ºE; 82ºNW faults and consist of quartz, arsenopyrite, pyrite, pyrrhotite, sphalerite, chalcopyrite, freieslebenite, semseyite, galena, jamesonite, polybasite, owyheeite, bournonite, boulangerite, freibergite, pyrargyrite, dolomite, ankerite, scorodite, anglesite, plattnerite, covellite, cerussite and pyromorphite. The mining activity took place between 1866 and 1973. About 3200 tons of galena and 3200 tons of sphalerite were exploited. The Castanheira stream crosses the mining area and discharges in the Douro river. Four mine dumps without any vegetation cover and composed by tailings are located over 2 km, along the Castanheira stream and its tributaries.

The BCR sequential extraction was applied to samples from tailings and sediments collected in Castanheira stream to assess the Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Sb and Zn fractionation. This method consists of three extraction steps (Quevauviller, 2002). A final residue and a separate sample were digested with *aqua regia* to determine the recovery. The quality of analytical data for the BCR procedure was assessed by carrying out analyses of the certified reference materials BCR-701 and BCR-143 for *aqua regia* digestion. The recovery ranges between 90 to 110 % for 90 % of elements and precision is better than 10%.

As, Cr, Mn, Ni and Sb were not extracted from oxidizable fraction, suggesting the complete weathering of sulphides. Sediments have higher Al, Cu, Fe, Mn, Pb and Zn contents in exchangeable and reducible fractions and arsenic in latter than tailings, suggesting leaching of those elements from tailings (with low pH <4.89) to sediments. Since the closure of the Terramonte mine, most sulphides from tailings were totally weathered. However, significant contents of Pb (up to 116.32 mg/kg), Zn (up to 22.28 mg/kg) and Fe (up to 1025 mg/kg) in the sulphide fraction suggest galena, sphalerite and pyrite occurrences, as samples do no contain organic matter (OM). Therefore, BCR procedure is a useful tool to predict the degree of sulphides weathering, namely in samples without OM.

Quevauviller, Ph. (2002). Methodologies in soil and sediment fractionation studies. Single and sequential extraction procedures. European commission, DG Research, Brussels, Belgium.

PT.40

Metal speciation conversion in urban soil redeposited in aqueous sludge

Bento DM[1], Mirlean N[1], Baisch P[1]
[1]FURG - Oc. Geológica

Urban soil highly polluted with heavy metals has been subjected to bath experiments to follow the change in metal speciation within the aquatic environment. It was found that labile fractions of Cu, Zn and Ni were reduced, while Cd and Pb bioavailability increased during the experiment. High levels of pollution and changes in speciation leading to urban soil redeposition in fluviolacustrian environments are a serious threat to aquatic organisms.

PT.41

Deployment of method for analysis of $\delta^{13}C$ (n-alkanes C_1-C^5) in gas samples at low concentrations.

Juliana Rozo Morales[1], Angela de Luca Wagener[1], Arthur de Lemos Scofield[1], Aida Pereira Baeta[1].
Laboratorio de Estudos Marinhos e Ambientais LABMAM. Departamento de Quimica PUC-Rio, juliana_rozo@hotmail.com

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The concentration and isotopic composition of gases (n-alkanes C_1-C_5) have been used successfully for interpretation of process involved in gas and oil formation. The isotopic composition provides valuable information about the source and type of natural gas (thermogenic, biogenic, mixture gas). In geochemical studies it is a challenge to determine the isotopic composition of gases at low concentration (<1000 ppm) due to poor sensitivity of the conventional technique (GC-IRMS). A new method was developed to overcome this limitation using a pre-concentration system (PreCon). This online system consists in selective trapping (using liquid nitrogen) of condensable hydrocarbons (C_{2+}, CO_2, N_2, O_2, N_2O, H_2O) while methane is oxidized, cryo-focused and injected in the GC-IRMS system. We tested some modifications in the analytical system to achieve sufficient accuracy and precision in the analysis of standard gas. The introduction of a PLOT column in the pre-concentration device (main trap) allowed reaching this goal. Likewise, the interferences were minimized using a trap cleaning and an oxidant (I_2O_5) for olefins removal. The combustion of gases C_{2+} was made in the GC-IRMS system while the methane was oxidized in the PreCon device. The method was tested analyzing the headspace of sediments and drilling samples with low concentrations of C_1-C_5 (2 -100 ppm C_1). The determination of the isotopic composition of these samples confirmed the applicability of the method with a high analytical precision (<0,5 ‰).

PT.42

Assessment of arsenic and chromium in residential dust under the potential influence of wood preservation activities

Maria Lucia Kolowski Rodrigues, Jovana Bavaresco, Mariana Vieira Coronas, Vera Maria Ferrão Vargas

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Dust is an important medium for the environmental dispersion of potentially toxic elements. Even after deposition it is an agent that integrates the contamination process in indoor environments. On the contrary of air or soils, whose constant renewal may dilute and mask the presence of contaminants, dust is a more long-term testimony to the history of human exposure in areas subject to atmospheric contamination. In this study, the concentration of arsenic and chromium was assessed in house dust samples, collected in a residential area adjacent to an old wood preservation plant. The old facility is located in Triunfo, state of Rio Grande do Sul, Brazil, and operated between 1960 and 2005, using CCA among other preservatives. The study is part of a research project developed by FEPAM, the environmental protection agency of Rio Grande do Sul State. Dust samples were collected by sweeping, in the attic of nine residences. A house that was geographically distant from the industrial area was selected as reference to compare the results. The analyses were performed in the Laboratory of Analytical Geochemistry/UNICAMP by inductively coupled plasma mass spectrometry (ICP/MS), after the samples were digested using the USEPA 3050b method. The results were validated by the analysis of reference materials. At the end of assessment, each residence was marked on a map of the area, according to the relative degree of dust contamination. For this purpose, a numerical index was used in association with a color scale, expressing the number of times the concentration of the element analyzed exceeded the reference value. The results indicated the following mean contents and respective ranges of variation of the elements assessed: arsenic – 11.0 (3.4 to 20.8) mg kg^{-1} and chromium - 25.7 (14.3 to 48.7) mg kg^{-1}. The spatialization of the data through the chromatic index pointed to the residences close to the plant entrance as those most affected by the deposition of contaminated dust. The contamination probably stems from the former management of inputs and treated wood, besides the circulation of vehicles on unpaved roads.

PT.43

ASSESSMENT of the relationship between δ18O freshwater sponge spicules and δ18O pond water for paleo-environmental purpose: a modern case study (Lagoa Verde, MG, Brazil).

MATTEUZZO M.C.[1], ALEXANDRE A.[2], SONZOGNI C.[2], VALLET-COULOMB C.[2], VARAJÃO A.F.D.C.[3], VOLKMER-RIBEIRO C.[4], ALMEIDA A.C.S.[5], VARAJÃO C.A.C.[3]
[1]Universidade Federal de Ouro Preto/Université Aix-Marseille III - DEGEO/CEREGE, [2]CEREGE/CNRS, [3]Universidade Federal de Ouro Preto - DEGEO, [4]Museu de Ciências Naturais/Fundação Zoobotânica do Rio Grande do Sul, [5]Instituto Federal de Minas Gerais/ Campus Ouro Preto

Several studies have demonstrated that biogenic silica particles such as diatoms and phytoliths precipitate in isotopic equilibrium with their forming water. In other words, their oxygen isotopic composition ($\delta^{18}O$) is related to both the $\delta^{18}O$ signature of the forming water and temperature. Fossil diatoms and phytoliths recovered from sediment can thus be used for paleoenvironmental reconstructions. Sponge spicules are amorphous silica particles widespread in freshwater environments and well preserved in sediments where they can account for several % of the dry weight (spongillites). In Minas Gerais (Brazil) spongillites constitute a reserve of 5.8 million tons scattered over a surface of about 45 km^2. Their age ranges from 3 to 28 kyrs BP. They are exploited for industrial purpose (ceramic). Although morphological assemblages of fossilized freshwater sponge spicules can be used for reconstructing paleohydrological parameters, their $\delta^{18}O$ signature has never been investigated. Here we aim to assess if modern lacustrine sponge spicules (*Metania spinata)* from a Minas Gerais pond, form in oxygen isotopic equilibrium with the pond water. For this purpose living sponges and pond water samples were collected during one year in Lagoa Verde (Minas Gerais). The water temperature was measured. Spicules were chemically purified (UFOP). They are currently being analyzed in $\delta^{18}O$, after a controlled isotopic exchange, by Laser-Fluorination-IRMS (CEREGE). Reproducibility of the measurements is equivalent to reproducibility obtained for phytoliths and diatoms (<0.3 per mil). Waters were analyzed in $\delta^{18}O$ and δD (CEREGE). The relationship between $\delta^{18}O_{spicule}$, $\delta^{18}O_{water}$ and temperature is examined.

PT.44

Pb, Nd and Sr Isotope Compositions of the Reference Material BRP-1 (Basalt Ribeirão Preto)

Babinski, M.[1], Ruiz, I.[1], Petronilho, L.[1], Enrich, G.[1], Souza, S.[1], Enzweiler, J.[2]
[1]Universidade de São Paulo - Centro de Pesquisas Geocronológicas, Instituto de Geociências,
[2]Universidade Estadual de Campinas - Instituto de Geociências

The geochemical reference material, Basalt Ribeirão Preto BRP-1 was issued with certified values for forty-four constituents, derived according ISO Guide 35 recommendations and the International Association of Geoanalysts (IAG) Protocol (Cotta & Enzweiler, 2008). Here we report the first isotopic data of Pb, Nd e Sr obtained for BRP-1, as well as, Pb, Nd, Sm, Rb and Sr mass fractions obtained by ID-TIMS (Isotope Dilution Thermal Ionization Mass Spectrometry) technique on this material. All analytical procedures were carried out at the Center of Geochronological Research, at University of São Paulo. Test portions of BRP-1 were dissolved using HF, HNO_3 and HCl acids, either in PFA vessels heated on hot plate or in Parr bombs, followed by element separation from matrix by ion exchange. The two of dissolution procedures produced similar results. The Pb isotope ratios obtained were: $^{206}Pb/^{204}Pb = 18.000 \pm 0.013$, $^{207}Pb/^{204}Pb = 15.532 \pm 0.011$, $^{208}Pb/^{204}Pb = 38.392 \pm 0.038$. These values are means and the uncertainties are one standard deviation of the mean of thirteen analyses. The mean of $^{143}Nd/^{144}Nd$ isotopic ratio obtained for seven replicates was 0.512359 ± 0.000021, and the average of $^{87}Sr/^{86}Sr$ ratios determined on nine replicates was 0.705995 ±0.000097. The mass fractions of elements used in isotope systematics, determined by ID-TIMS yielded the following results: Pb = 5.273 ±0.076 $\mu g.g^{-1}$ (n=9), Rb = 36.195 ±0.013 $\mu g.g^{-1}$ (n=4), Sr = 501.16 ±0.94 $\mu g.g^{-1}$ (n=5), Sm= 10.779 ±0.017 $\mu g.g^{-1}$ (n=4), Nd = 52.000 ±0.131 $\mu g.g^{-1}$ (n=4). These values are means and the uncertainties are one standard deviation of the mean, and agree with the certified values within the 95% confidence level. These isotopic data are still a small dataset and a much larger number of analysis is needed, but the precision indicates that BRP-1 (Basalt Ribeirão Preto) can be also used as reference material for isotope ratio measurements.

Cotta A.J.B. and Enzweiler J. (2008) Certificate of Analysis of the Reference Material BRP-1 (Basalt Ribeirão Preto). Geostandards and Geoanalytical Research 32:231-235.

PT.45

Multi-element determinations in oil shale and soil samples by instrumental neutron activation analysis

M. Saiki[1], H. Rech[2], A. B. Ferreira[3], F. A. Genezini[4], P. H. N. Saldiva[5]
[1]Instituto de Pesquisas Energéticas e Nculeares -IPEN-CNEN/SP - Centro do Reator de Pesquisas, [2]Universidade Federal do Pampa - UNIPAMPA - Engenharia de Energias Renováveis e Ambiente, [3]Instituto de Tecnologia e Pesquisa de Segipe - GATEC, [4]Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN/SP - Centro do Reator de Pesquisas, [5]Faculdade de Medicina da Universidade de São Paulo - Departamento de Patologia

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Oil shale is an organic-rich fine-grained sedimentary rock that has received much attention over the last years as an alternative energy source. The analysis for element distribution in raw shale is highly important for its exploration and processing programs as well as for studying its formation and the dispersion of its potentially toxic elements. In this study, instrumental neutron activation analysis (INAA) procedure was established for the multi-element determinations in oil shale and soil samples from Irati oil shale in São Mateus do Sul, Parana, Brazil. Oil shale from upper and lower layers, retorted and fine shale were ground to a powder and aliquots of each sample and element standards were irradiated for 8 h under a thermal neutron flux of about 4.0 x 10^{12} n cm^{-2} s^{-1} of the IEA-R1 nuclear research reactor. After adequate decay times the induced gamma activities were measured using a gamma ray spectrometer. Comparisons made between the results showed higher concentrations of As, Ba, Co, Fe, K, Rb and Zn in shale oil samples than those presented in soil. However concentrations of Br, Cr, Cs, Hf, Sb, Th, U and lanthanide elements present in oil shale samples were lower than in soil or the same order of magnitude. Quality control of analytical results was performed by analyzing two certified reference material NIST 2704 Buffalo River Sediment and IAEA Soil-7, whose results presented good precision and accuracy. These preliminary results demonstrated that INAA can be a useful tool for the evaluation of shale oil element composition.

PT.46

Choosing the right ICP for the geoanalytical task

Simon Chenery, Jennifer Cook, Matthew Horstwood and Michael Watts
Environmental and Isotope Geochemical Laboratories, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

The geoscience laboratories at the British Geological Survey are equipped with a unique range of ICP spectrometers, from ICP-AES through conventional quadrupole ICP-MS to multi-collector ICP-MS. The presentation examines a number of applications and describes why a particular instrument was selected as the most appropriate to perform the analytical geochemical task. Examples included: (i) highly saline matrices analysed on a Spectro Blue ICP-AES instrument; (ii) arsenic speciation in environmental matrices by Agilent 7500 quadrupole ICP-MS; (iii) mapping marine bio-structures by laser ablation coupled to a Nu Attom single collector magnetic sector ICP-MS instrument and (iv) silicon isotope ratios in waters using a Thermo Neptune multi-collector ICP-MS instrument. The aim is to highlight the factors that the analyst should take into consideration when deciding which ICP system to choose for a particular task, including sample type, speed or cost of analysis, detection limits required for the application, together with accuracy and precision.

PT.47

Evaluating Holding Time for Stable Pb Isotope Analyses in Groundwater Samples

Martins VTS[1], Babnski M[1], Ruis IR[1]
[1]University of São Paulo - Geoscience Institute

Tracing groundwater contamination is an important part of the assessment and management of water resources. Pb isotopes have been used as environmental indicators of water contamination and may help identify the contamination sources. A very important part of these studies success is the care during collection, preservation and storage of the samples, in order to avoid cross contamination and ensure the validity of the results. Some inorganic chemical parameters in water have an expiration date of hours, days or months, but there is no information available for Pb isotopes. In order to evaluate the holding time for Pb isotopes analyses in groundwater samples, samples collected from the same well were analyzed, after storage for three different periods (1 day, 1 month and seven years). All samples were collected by low flow method, in low-density linear polyethylene 500 mL bottles that had been previously cleaned by acid washing techniques. During field sampling, bottles were rinsed three times with sample water before collection. Filtration was done less than 10 hours after collection at the laboratory under a class-100 laminar flow hood, using an acid cleaned polysulfone filter holder with receiver connected to a vacuum line. Cellulose acetate membranes of 0,45 mm and 47 mm diameter were used. The results showed that the Pb isotopic ratios do not vary with time. The $^{207}Pb/^{206}Pb$ ratio for the sample stored for 1 day is 0.866, which is the same ratio obtained for the samples stored for 1 month and seven years. The $^{208}Pb/^{206}Pb$ ratios present a small variation, between 2.101 and 2.104, which is lower than the standard deviation average for these samples. Lead concentrations for samples collected in October and December are between 0.203 and 0.261 µg/L, whereas samples collected in April pointed value between 0.467 and 0.516 µg/L. The sample collected in December 2004 was analyzed one year and four months later and then seven years later. These results showed that occurred an increment of less 23%, indicating that the holding time may influence the lead concentration, but does not interfere on the Pb stable isotopic ratios.

PT.48

Trace metal and rare-earth elements in a sediment profile from the Rio Grande reservoir, São Paulo, Brazil, by INAA

Franklin, R.L.[1], Deborah I T Favaro, Damatto, S.R.[2]
[1]CETESB /SP - Laboratório de Química Inorgânica (TLAI), [2]IPEN/CNEN-SP - Laboratório de Radiometria Ambiental – CMR

The Rio Grande Reservoir, located in the southeast of the Sao Paulo Metropolitan Area, supplies water for four counties (about 1.6 million people). This reservoir has been seriously affected by urban expansion due to chaotic urban occupation. It also suffers from a large amount of untreated domestic and industrial sewage and waste released directly into the reservoir. In this study, a 0.40 m sediment core was collected near the catchment point of the water supply, sliced into 2 cm layers (20 samples) and dated by the ^{210}Pb method. Samples were air dried at 20–25 °C, passed through a 2 mm sieve, ground in a mortar and then homogenized before analysis. The samples were then submitted to instrumental neutron activation analysis (INAA) in the IEA-R1 nuclear research reactor at IPEN and As, Ba, Ca, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb were determined. The uncertainties of the results were calculated by error propagation. The validation of the methodology for precision and accuracy was verified by measuring the reference materials SL 1 (Lake Sediment 1, IAEA), Soil 5 (IAEA) and BEN (Basalt–IWG-GIT). The enrichment factor (EF) was calculated using the concentrations in the deeper layer of this profile as reference values and Sc as a normalizing element (range value 17.9 to 22.1 $mg\ kg^{-1}$, median 20.2 ± 1.0). Significant enrichment ($1.5<EF<5.5$) was found for Zn, Na, La and Sb in the upper layers. For Sm and Fe no significant enrichment ($1.0< EF <1.5$) along the sediment profile was observed. For the other elements (Ce, Hf, Lu, Rb, Ta, Tb and Yb) the enrichment occurred in the deeper layers or along the profile and showed depleted levels in the upper layers. The elements Cr and U presented enrichment ($1.0< EF <1.5$) in the middle of the sediment profile, with upper and deeper layers presenting lower concentrations. From the data obtained in the present study it was possible to trace the history of pollution by some metals and trace elements in this reservoir for approximately the last 50 years.

PT.49

Chemical characterization of Geological materials: Validation of an analytical methodology for Rare Earth Elements determination by ICP-QMS

Rui Santos
LNEG - Portugal

An analytical methodology for REE quantification by ICP-QMS, employing the PQ Excell spectrometer, was developed. Sintering with sodium peroxide (Na_2O_2) at 480 ºC was used for sample decomposition. Numeric coefficients for polyatomic interferences corrections were experimentally evaluated. The methodology has been validated by analysis of 5 geological CRM and 9 proficiency testing samples (*GeoPT Programme*). Precision was better than 10% and mean recoveries of 100±5% for all REE except Gd, were obtained. The minimization of random and systematic errors has been achieved and therefore analytical results present the required quality for petrogenetic studies.

PT.50

Heavy metals contents of some common used fertilizers in Saudi Arabia

AlHorayess O[1], Albokari MM[2], Alhobaib A[2]
[1]King Abdulaziz City for Science and Technology (KACST) - National Centre for the management of radioactive waste, [2]King Abdulaziz City for Science and Technology (KACST) - Atomic Energy Research Institute (AERI)

A wide range of fertilizers are used in Saudi Arabia. Most fertilizers producing companies only mention the main components on the pack of their product. They usually indicate the content of other elements as "other additives". In this study, 24 industrial fertilizer samples collected from the Saudi market were analyzed for assessment of heavy metals concentrations. The samples were analyzed using NAA and ICP-MS techniques. The results obtained show concentrations of heavy metals with considerable differences between the 24 fertilizers samples. This increases the need for more investigations for the purpose of human and environment protection.

PT.51

Use the technique of diffusive gradients in thin films (DGT) for measurement of Cu and Ni in Negro river - Amazon Basin – Brazil

Yabuki L. N. M.[1], Colaço C. D.[1], Pedrobom J. H.[1], Menegário A. A.[1], Domingos R. N.[1], Pascoaloto D.[2]
[1]Universidade Estadual Paulista - UNESP - Centro de Estudos Ambientais - CEA, [2]Instituto Nacional de Pesquisa da Amazônia - INPA - Coordenação de Pesquisa em Clima e Recursos Hídricos - CPCRH

The technique of diffusive gradients in thin films (DGT) allows to measure *in situ* the labile metals in freshwater[1]. This technique is based on the 1st Fick's law, which establishes a constant metal flow though a diffusive layer for a given concentration gradient.

Due to the complexity of using DGT, specifically for samples from the Amazon region (low ionic strength and high organic matter) a new analytical procedure is proposed. The procedure is based on the determination of an apparent diffusion coefficient (D_{ap}) in laboratory by deployments in a similar matrix to that site of study. The D_{ap} determined is then used for *in situ* measurements.

Samples were collected in Negro river (Manaus AM, Brazil). The DGT device was assembled with agarose-polyacrylamide hydrogel as diffusion layer (conventional pore) and Chelex-100 resin (supported on the same gel) as ligand. The analytes were eluted with 1 mol L^{-1} HNO_3 and subsequently determined by inductively coupled plasma mass spectrometry (ICP-MS).

Deployment curves of Cu and Ni were satisfactorily linear, characterized by an R^2 of 0,626 for Cu and R^2 of 0,944 for Ni, showing that the diffusion process followed the 1st Fick's law. From the labile metal concentration in the sample (determined by solid phase extraction), the obtained D_{ap} values were $1{,}24.10^{-5}$ and $2{,}06.10^{-5}$ $cm^2 s^{-1}$ (23,8 °C) for Cu and Ni, respectively. These values were considerably lower than the conventional value ($6{,}23.10^{-6}$ and $5{,}77.10^{-5}$ cm^2 s^{-1}) for solutions with ionic strength > 0.1 mmol L^{-1}, showing the significant effects in the determination of metals in these samples due to low ionic strength and/or high content in organic matter.

By using the proposed approach, concentrations of 0.08 ± 0,07 µg mL^{-1} and 0.28 ± 0.05 µg mL^{-1} were obtained for *in situ* determinations of Cu and Ni, respectively. These results were consistent with expected values.

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PT.52

In situ determination of labile mercury in river Ribeirão Claro - SP using DGT technique.

Colaço CD[1], Menegário AA[2], Yabuki LNM[1], Oliveira RLF[1], Alcântara AL[2]
[1]Unesp - Instituto de Geociências e Ciências Exatas, [2]Unesp - Centro de Estudos Ambientais

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The investigation of the bioavailability of metals in water is as important as the knowledge of their concentration when considering the environmental impact. The most studied of the toxic metals is the mercury (Hg), which has mutagenic properties and is easily volatized. The free ion metal or labile metal species (in solution) are the form of metal that often accumulate in aquatic organisms. In addition, toxicity, distribution and mobility of a metal are related directly with the chemical species present in the environment. The labile fraction can be present in aquatic systems in very low concentrations, making difficult its determination by analytical techniques. In the last two decades, passive sampling techniques have become a promising tool for environmental analysis. Among these techniques, the diffusive gradients in thin films (DGT) technique is notable because it allows measure quantitatively *in situ* the labile soluble metals in the aquatic systems and the preconcentration of analytes. The aim of this study was to determine the labile fraction of mercury in river Ribeirão Claro, SP by using the diffusive gradient in thin films technique – DGT. DGT samplers were assembled with P 81 membrane (cellulose phosphate) as binding phase and agarose gel as diffusive phase. Samples were collected in September (late dry season) and February (end of rainy season). Despite the Hg low concentrations, the quantification of labile fraction was possible due the ability of pre-concentration provided by DGT technique.

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PT.53

Hydrogeology and hydrochemistry of a karstic aquifer from Bonito, Mato Grosso do Sul State, Western region of Brazil

Gabas[1], Lastoria[1], Núbia G.P.Enetério[2], Aline A. Souza[2]
[1]Universidade Federal de Mato Grosso do Sul - Centro de Ciências Exatas e Tecnológicas,
[2]Universidade Federal de Mato Grosso do Sul - Centro de Ciências Exatas e Tecnológicas/PGTA

The karstic aquifer present in Mato Grosso do Sul State is composed by Precambrian carbonate rocks from Paraguay Belt, cropping out in the southwest region of the state, called Serra da Bodoquena. Despite hosting large amounts of groundwater resources, maintaining highly diverse groundwater-dependent ecosystems, and being the water supply system for urban and rural areas, this karst aquifer has not been hydrochemically characterized yet. A hydrogeological and hydrochemical study was conducted on a shallow karst aquifer in the urban area of Bonito County. Major parameters for hydrogeochemical classification were analyzed in UNESP´s Hidrogeology and Hidrochemical Laboratory in Rio Claro, SP. The results show that the groundwater is predominately calcium and magnesium mineralized and is classified as Ca-Mg-HCO_3 type. Water pH values range from 6.64 to 7.43 and electrical conductivity, from 317 to 827 µS/cm. The temperatures of water vary from 25.0 to 26.5ºC and the temperature of air, from 24.0 to 27.5 °C. Water from a deep well was classified as Mg-HCO_3 with electrical conductivity of 530 µS/cm. The groundwater flow direction in the studied area drives from west to east. However, extensive survey should be conducted to better characterize the regional groundwater flow, hydrochemistry and the relation between groundwater and surface water. The mechanisms that might be responsible for groundwater evolution in the area are dissolution of carbonate minerals from carbonate rocks and silicate minerals hydrolysis from siliciclastic metamorphic rocks from Cuiabá Group. Although, urban activities and business in rural areas should not be neglected as potential contamination source in a fractured aquifer, where recharge velocities are usually high. We also think groundwater vulnerability in this aquifer should be evaluated to guide management actions to guarantee public health and economic development of this region.

PT.54

Metals in soils adjacent to avenues of highly dense traffic in São Paulo city, Brazil

Ribeiro AP[1], Figueiredo AMG[1], Figueira RCL[2], Ticianelli RB[1]
[1]Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, Brazil., [2]Instituto Oceanográfico - Universidade de São Paulo, Pça. do Oceanográfico, 191, 05508-900, São Paulo, Brazil.

São Paulo is the largest city in Brazil with about 20 millions inhabitants in the metropolitan area, strong industrial activity and more than 9 million motor vehicles, which are responsible for increasing pollution in the region. Nevertheless, there is little information on metal contents in the metropolitan region soils. The presence of metal contaminants in the urban environment, particularly in urban soils, and the proximity to city inhabitants can cause harmful exposure to metals through inhalation, ingestion, and dermal contact. The present study aimed to determine Pb, Cu, Ni and Mo concentrations in soils along the most important traffic arteries of São Paulo city. These metals are usually associated with high traffic densities, originating from exhaust emissions, tire, braking, vehicle and engine wear, and/or the re-suspension of road dusts. Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) after ultrasound-assisted *acqua regia* leaching was employed as analytical technique. The concentration levels obtained ranged from 32 to 108 mg kg^{-1} for Pb and 39 to 260 mg kg^{-1} for Cu. These values exceeded international and São Paulo soil guiding target values, indicating a vehicular source. For Ni the levels ranged from 6 to 20 mg kg^{-1} and for Mo from 1 to 3 mg kg^{-1}, which are within the international and São Paulo reference values.

PT.55

Inventory of ^{137}Cs in marine sediments of Admiralty Bay, King George Island, Antarctica

Andreza P. Ribeiro[1,2], Paulo A. L. Ferreira[1], Mylene G. Nascimento[3], César C. Martins[3], Paula G. C. Amaral[1], Michel M. Mahiques[1], Rosalinda C. Montone[1], Rubens C. L. Figueira[1]

[1]Instituto Oceanográfico - Universidade de São Paulo, Pça. do Oceanográfico, 191, 05508-900, São Paulo, Brazil, Pça. do Oceanográfico, 191, 05508-900, São Paulo, Brazil

[2]Universidade Nove de Julho, Diretoria da Saúde, Rua Vergueiro, 235, 01505-001, São Paulo, Brazil

[3]Centro de Estudos do Mar - Universidade Federal do Paraná, Av. Beira-mar, no number, Balneário Pontal do Sul, Pontal do Paraná, PR, Brazil.

In the context of radioactivity contamination, ^{137}Cs is a hazardous nuclide with high yield in ^{235}U fission, which is a main component of nuclear warheads, and is globally present in the diverse ecosystems on Earth. Establishing its reference inventory is critical for the estimation of future impacts of radioactive pollution in a remote environment such as Antarctica as well as to help understanding dynamic marine processes of which ^{137}Cs can serve as a tracer. Accordingly, this work determined the reference inventory of the radionuclide ^{137}Cs of Admiralty Bay (Antarctica) in five recent sediment profiles through the means of high-resolution gamma ray spectrometry. The obtained reference inventory was 20.23 ± 8.94 Bq m^{-2} indicating low ^{137}Cs ambient activity for this site. Furthermore, a model of diffusion-convection of ^{137}Cs in sediments was applied to evaluate some insights about its behavior in Admiralty Bay. The model produced results that showed significant correlation between the reference inventory and the initial input of the nuclide in the system due to the global fallout of past nuclear tests and expected values of local sedimentation rates. It also highlighted the relevance of accounting the vertical diffusion of ^{137}Cs and its residence time in the sediment source area before deposition when studying it or using ^{137}Cs as a tracer for environmental processes.

PT.56

Natural and artificial radionuclides distribution in the Cananéia-Iguape estuarine system (São Paulo, Brazil)

Paulo Alves de Lima Ferreira, Andreza Portella Ribeiro, Keila Tramonte Monteiro, Elvis Joacir de França, Rubens Cesar Lopes Figueira

With the advent of techniques that enabled the detection of radioactivity, a new frontier was opened in the many areas of Earth sciences, as the radionuclides can be used as tracers for processes of physical, chemical and biological natures. In this context, natural (^{40}K, ^{232}Th and ^{238}U) and artificial (^{137}Cs) radionuclides were measured through the means of high-resolution gamma spectrometry, a non-destructive technique, in the Cananéia-Iguape estuarine system (São Paulo, Brazil). The activities obtained are 107.61 – 573.84 Bq kg^{-1} for ^{40}K, 11.11 – 73.65 Bq kg^{-1} for ^{232}Th, 2.27 – 60.76 Bq kg^{-1} for ^{238}U, and 0.23 – 3.49 Bq kg^{-1} for ^{137}Cs. These radionuclides showed significant ($\alpha = 0.05$) correlation with grain size distribution, carbonate fraction and organic carbon content.

PT.57

Microbial Community associated with Black Powder in Natural Gas Pipelines

Albokari MM[1], Ibrahim A[2], Alkhomshi N[1], Alhobaib A[1]
[1]King Abdulaziz City for Science and Technology (KACST) - Atomic Energy Research Institute (AERI), [2]Saudi Aramco

Biological analysis based on PCR and clone library approaches, along with physical analytical techniques (XRD, XRF, γ-Spectrometry) were used to characterise 'black powder', a major constituent of the environmentally hazardous wastes generated from the natural gas industry. Black powder is a very complex material, containing hydrocarbons, sulfates, iron oxides, heavy metals, mercury and range of cations and anions. In addition, a microbial community can be associated with the material. It is important to understand the risks and potential environmental impacts of black powder and characterising black powder is a necessary first step in doing so. One sample was collected from a natural sales gas pipeline, and 16S DNA sequenced to characterise the microbial community. The most frequently encountered bacterial species were identified as iron-reducing bacteria (48%) and phenol- and carbon-reducing bacteria (38%), which dominate the microbial consortium. Magnetite (Fe_3O_4) was the most abundant mineral phase, while gamma spectroscopy did not show any unusual radioactivity content.

PT.58

Removal of Uranyl Ions from Aqueous Solutions by Barium Titanate

AL-Hobaib AS[1], AL-Suhybani AA[2], AL-Homaidy KA[2], Albokari MM[1]
[1]King Abdulaziz City for Science and Technology (KACST) - Atomic Energy Research Institute (AERI), [2]King Saud University - Faculty of Science, Chemistry Department

This article deals with the preparation, characterization and the use of inorganic ion exchangers that have the ability to adsorb some radionuclides. In order to obtain ion exchangers useful in the disposal of radioactive waste, barium titanate ($BaTiO_3$) was prepared in different conditions, followed by a study of some physical properties such as surface area and grain size and the size of pores on the surface of ion exchanger. It was then used as an adsorbent material for uranium ions with the study of all factors affecting the adsorption processes such as time, temperature and the competing added ions. In this study, the measurement of uranium concentration of was carried out using an UV/Vis spectrophotometric method. Kinetic equations were also applied to the adsorption process of uranium in order to understand the reaction kinetics. It was found that the inferred mechanism is a particle spreading with a limited contribution of mechanical spread of membrane. Also the values of dynamic variables and thermodynamics were determined and it was found that the adsorption process follows first order rate kinetics. Both Freundlich and Langmuir adsorption models well applicable to the considered system.

PT.59

Three-Dimensional Subsurface Realizations of Soil Property Distribution: A Case Study from an Arid Site

Roig, C[1], Haugen, B.D.[2]
[1]U.S. Army Engineer and Development Center - Geotechnical and Structures Laboratory, [2]URS Corporation

Three-dimensional representations of geologic environments are difficult because of the variability and heterogeneity of the various soil properties that characterize them. Furthermore, such difficulty is exacerbated due to limited soil sampling and data collection. This is especially true in remote areas and in various developing countries. A process that utilizes remotely sensed data, regional geologic information, and limited field-sampled soil data to define the geologic architecture of a site (i.e., the size, shape, and distribution of soil features resulting from their geologic origin) was developed and applied to an arid site in southern California, U.S.A. A conceptual model that included multiple geologically-plausible realizations of the distribution of soil materials and associated properties was created. Multiple subsurface realizations were developed in an iterative process using the Transmission-Probability Geostatistics (T-PROGS) module of the Department of Defense Groundwater Modeling System. T-PROGS is an indicator-based stochastic simulator that uses a transition-probability-based geostatistical approach to model the occurrence of geologic materials in a given 3-D space. Four geologic materials, with variations in soil properties, were defined using limited "hard" data from two soil trenches. Forty-two synthetic borehole logs were created using field notes, published and unpublished geologic information, and hard data. The combined set of 44 (two containing real data from trenches and 44 synthetic) borehole logs were used as base data for all of the realizations produced with T-PROGS.

The resulting model accurately portrayed on-site geologic conditions from sub-centimeter to multi-meter scales. The method produces 3-D models that are statistically reproducible, technically defensible, and closer to reality than assumptions of uniform material properties. Other more traditional statistical methods are less effective for developing realistic models, because they fail to capture asymmetric juxtapositional tendencies (e.g., fining upward sequences, cross-cutting layers, lenses, etc.). The method does not function on a curvilinear transitional relationship between materials. That is, distinct non-gradational material boundaries and transitions can be determined.

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PT.60

Transient and stationary solutions of the heat diffusion equation for a natural reactor and the variability of the Earth's magnetic field

V.M. de Aquino[1,2], H. Iwamoto[3], B. C. Amorim
[1]UEL, [2]Departamento de Física, [3]UEL - Departamento de Física

The Earth's magnetic field presents variability in its intensity and direction that does not seem compatible with some conventional energy sources proposed to explain its production. An alternative was proposed by Herndon in 1993 and consist of a natural reactor at the center of the Earth. The plausibility of this proposal has been analyzed through the use of numerical simulations and a low flux of antineutrinos from decay of fission products generated during nuclear reactions has been estimated. Indications of some flux of antineutrinos from a source in the center of the Earth could support the Herndon's hypothesis. Due to the prevision of low flow of antineutrinos, and the difficulty to detect these particles, the hypothesis of existence this reactor can hardly be verified by this method. An alternative would be to associate variations in Earth's magnetic field with theoretical previsions in the power of the proposed source.

The measurements of the geomagnetic field show a pattern of variability that suggests the separation in different classes, short, medium and long term. The dynamics of a nuclear reactor depends on its reactivity. There are several factors that influence the reactivity of a reactor, three of them have characteristic times which can be directly associated with variations in the power of the reactor. 1) The set of physical properties of the fuel mass, which determines the diffusion time of neutrons. 2) The amount of poison, elements generated during nuclear reactions, which depend of certain time constants of these elements. 3) The temperature, which can function as a mechanism on and off with a characteristic time which can be estimated from the knowledge of the transient solution to processes of cooling in the reactor.

In this work, for a reactor with the characteristics proposed by Herndon, the neutron diffusion time, the characteristic times of poisons and the time associated with heating of an isolated reactor are compared and the arguments to associate the time of cooling to one of patterns of variability in the power of the reactor are presented.

PT.61

Field Measurement Positioning Systems and Geostandards

Rybansky M[1,2], Kratochvil V
[1]University of Defence - Military Geography and Meteorology, [2]University of Defence in Brno - Military Geography and Meteorology

This article summarizes the various expressions of field object positioning using different coordinate data and different methods, such as use of maps, exploiting the properties of digital Global System for Mobile Communications (GSM) networks, Global Navigational Satellite Systems (GNSS), Inertial Navigation Systems (INS), Inertial Measurement Systems (IMS), hybrid methods and non-contact (remote sensing) methods; all with varying level of accuracy.

Another way to determine the location of geographic objects is by using different geographical identifiers, gazetteers and descriptive methods that are specific to each class of elements. The starting point for determining the format of these is the standardization agreement (ISO 19112, 2003), which is the basic framework for applying geographical identifiers.

For each class of objects (e.g. geological areas, topographical relief, bodies of water, vegetation, settlements, roads, etc.) there is a hierarchy of geographic location identifiers, which may supplement or replace coordinate identification. The classes of geographical objects and the methods of using their geographical location identifiers and descriptive characteristics are listed in paper.

PT.62

Anomalous geochemical fields of Au-Ag ore-forming systems of the Northern Priokhotje (Russia)

Raisa Kravtsova, Artem Makshakov
Institute of Geochemistry, Siberian Branch of the RAS,
[1]a Favorsky Str., Irkutsk, 664033 Russia, pavpla@igc.irk.ru

The endogenous and exogenous anomalous geochemical fields (AGF), comprising primary haloes and secondary haloes plus sediment streams accordingly, were studied within largest Au-Ag regions of the Northern Priokhotje. The full-scale geochemical mapping allowed investigating AGF for every type of ore mineralization – Au-Ag, Ag-Pb, Sn-Ag and Sn. These maps illustrate the regularities in spatial distribution of the element associations. Within regional and local Au-Ag ore-forming systems that are the ore-magmatic systems and the deposits accordingly, the comparison of primary and secondary haloes and streams indicates the uniformity of their composition and regular decrease in field contrast range in the following order: primary halo – secondary halo – sediment stream.

AGF ascertained by streams are characterized with some negative features such as low contrast, common spreading, and disturbances of quantitative correlations. Nevertheless, this kind of survey has some advantages such as simplicity, rapidity, relative sampling depth, and capability to collecting information rapidly about the metallogenic features of the region in whole. These peculiarities are frankly in the composition and structure of exogenous AGF exposed with the secondary haloes. The comparison of exogenous AGF with endogenous AGF shows that the exogenous zonality directly related with endogenous one. A serious disadvantage of the method is low informativity of the secondary haloes in the case of the isolated area. The secondary haloes are practically ineffective for prospecting when the layer of friable deposits comes up to 0.4-0.5 m.

Thus, theory and practice of geochemical prospecting should account for the features of AGF formation within the regional ore forming system in whole. The small- and middle-scale geochemical survey is the exclusive method that allows appreciating the considerably large areas under geochemical projecting and prospecting.

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PT.63

Characteristics of the Tungsten-Lithium (W-Li) mineralization and mineral processing of the Arbayan deposit, Mongolia

T. Altantsetseg[1], B. Enkbat[1], L. Batzorig[1] and N.Tsengelbayar[2]
[1] *Central Geological Laboratory (CGL), Mongolia*
[2] *Oyuni undraa LLC, Mongolia*

Lithium is the lightest metal and the yearly consumption of more than 100000 t LCE is likely to increase tremendously (10-20%) alongside with the development of electro driven cars. World reserves are estimated to be 20 Mt.

The Arbayan **W-Li** deposit, hosted in the medium-late jurassic granitoid Sharkhad formation **(γ_2 J_{2-3} s)** is located in the Sukhbaatar province, Eastern Mongolia. The mineralization is related to a pneumatolytic and hydrothermal alteration (greisenization) of Granite. The average ore content of the deposit is estimated to be 56.14Mt with LiO_2 concentrations ranging from 0.39% to 1% and average WO_3 concentrations of 0.14%. Thus this deposit represents worldwide one of the prospective locations where lithium is linked to a tungsten ore mineralization. This study aimed to investigate the host rocks, the mineral chemistry, the hydrothermal alteration, the mineralization and the technological mineralogy of tungsten and lithium.

Existing drill cores of the deposit were used to take representative samples for this study. Analytical techniques like microscopy, XRD, ICP-OES, MLA, LA-ICP-MS and Automated Mineralogical Analysis were applied at Central Geological Laboratory of Mongolia, Geological Survey of Finland, AMMTEC of Australia and Clausthal University of Technology, Germany to investigate particular aspects of the deposit.

As results, three types of host-rock granites could be distinguished: (1) Greisenized and mineralized medium-coarse grained granite, (2) Greisenized fine grained granite, (3) Topaz-mica-quartz greisens by granite. Major ore minerals were identified as hubnerite, sphalerite, galena, chalcopyrite, pyrite, covellite, tennantite and molybdenite associating mainly to quartz and mica. With the identification of zinnwaldite as lithium hosting mineral, one of the main goals of this study was reached. By quantitative elemental analyses W, Zn, Pb, Cu and Mo were identified as major ore elements, accompanied by rather high concentrations of Li, Rb and Cs.

During this study, Tungsten- and Lithium- minerals were concentrated considerably from the ore by several types of mineral processing tests.

Due to the highly interesting elemental constellation, the ore was included in the CGL certification program for reference materials (CRM).

PT.64

Levels of metals and semimetals in sedimentary cores in Bertioga Channel, Brazil

Sartoretto RJ[1], Figueira RCL[1]
[1]Instituto Oceanográfico da Universidade de São Paulo

The Baixada Santista is one of the most exploited and populated regions of São Paulo state. During the last decades, due to intense industrialization the Baixada Santista has passed through a strong process of environmental degradation. Metals in sediments are persistent, present toxicity in varied concentrations and may be deposited reaching biota habitats. In this context, high concentrations of metals are of environmental concern to coastal management. The objective of this study was to characterize the concentration of the following metals at Bertioga Channel sediments: Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sc, V and Zn. Five sediment cores were sampled along the channel and analyzed. Determination of metals' concentrations was based on methods SW 846 US EPA 3050B and EPA 7471A. High As concentrations were obtained for at all cores, with considerable concentration similarity between the first and second sampling points. Analytical results showed that cores Bertioga 4 and Bertioga 5 have accumulated high quantity of metals and semimetals, mainly As, Cd e Cr. Normalization of concentration values showed low contamination at the cores. Nevertheless, As and Hg values indicated moderate to significant contamination at a few sampling points. Despite of the low probability of contamination demonstrated by the normalized values, an increasing at the sediment surface in EF, PLI and SPI parameters were observed. This might indicate processes of industrialization and environmental degradation acting in the region for the last decades.

PT.65

Contamination acquired during routine grinding of geologic samples

Jose Paulo Sertek(1), Sandra Andrade(1), Horstpeter Ulbrich(1)
(1) Instituto de Geociências – USP – Rua do Lago, 562 – Cep.: 05508-080- São Paulo, SP, Brasil,
email: jpsertek@usp.br

Contamination levels for a wide spectrum of elements were examined, acquired during routine grinding of geologic samples. Quartz crystals were the starting material, because of its rather simple composition and hardness (hence, easier ways to detect contamination, stronger interactions with grinding surfaces).

Powder samples (less than 200 mesh) were obtained following routines: number 1 initiated with crushing of crystals to manageable sizes by Fe-Mn steel jaw crusher, quartered and powdered by a Fritsch agate planetary mill. Another batch was prepared using a WC secondary crusher, and then finally powdered with the same agate mill. A third batch, also powdered with the agate mill, was crushed with a hydraulic press with Carbon steel plates. A second routine repeated the above described procedures, substituting the agate mill by a WC planetary Fritsch mill. The third routine followed the same procedures outlined, using now for the final powdering a Fritsch Cr-Fe steel planetary mill. Nine different powdered samples were thus obtained, prepared for analysis by conventional methods (solutions) and analysed preliminarily by semiquantitative ICP-MS procedures (TotalQuant, in triplicate). Those elements which showed significant contamination were further analysed either with ICP-MS or ICP-OES standard methods, while those that showed no response (intensities below, or close to, detection levels, such as all REE) were disregarded. Results show, not surprisingly, significant contamination with Cr-Fe routine: Fe (2400-3400), Cr (380-320), Cu (7-8), Ni (7-4), and V (1.6 to 2.1, all ppm), and with the WC routine: Co (82 to 75), W (950-1000), Mo (2-4) Ta (around 2.5) and Nb (around 0.7, all ppm). Contamination with agate grinding was in general negligible.

These studies were extended to determine cross contamination effects, first grinding a reference sample of basalt, followed by routine cleaning, and finally grinding of quartz, as depicted above (a similar procedure was used for cross contamination studies with a reference granite). Cross contamination effects on quartz were found negligible both for basalt and granite, except the ones already identified during primary contamination, as described in the cited routines.

PT.66

A Lower Dilution Fusion Technique for the Analysis of Phosphate Ores

WANG Yi-ya, XU Jun-yu, ZHAN Xiu-chun, QU Wen-jun
National Research Center for Geoanalysis, Beijing 100037, China

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A lower dilution fusion (LERDF) technique using a 5:1 flux-to-sample ratio has been developed for the accurate determination of 12 major, minor and trace elements in phosphate ores by wavelength–dispersive X-ray fluorescence spectrometry (XRFS). The choice of dilution ratio, fusion temperature, fusing time and quantity of releasing agent was discussed. The dilution ratio to the effect of F fluorescence intensities was investigated. For F analysis in phosphate ores, the LERDF technique ensures the higher fluorescence intensities and provides the accurate analytical values and the lower limit of determination. Instrument conditions, including corrections for spectral line interferences, were reported for 12 elements. Calibration was carried out using Chinese National Standard Materials, management samples and other samples, with similar matrix elemental compositions to phosphate ores. The matrix effect was corrected using experience coefficient method. The method precision (RSD, n=10) of F is 1.96% and 4.11%, corresponding to F contents of 3.54% and 0.61%, respectively, the precision of Ti, Mn and Na with lower content is 4.99%,3.39% and 1.58% respectively; the precision values of Mg, Al, Si, P, K, Ca, Fe and Sr, are all lower than 1.00%. The detection limit of F is 1140 µg/g. Applied to the phosphate ores, all the data were in agreement with reference or recommended values. It is necessary to determine bead samples immediately or, if not, place bead samples in dryer in order to ensure the accuracy of determination of F.

PT.67

Estimate of uncertainty of results of major and minor elements in silicate rocks measured by XRF

Vendemiatto MA[1], Enzweiler J[1]
[1]Universidade Estadual de Campinas - Unicamp - DGRN/IG

An analytical result should be accompanied by the measurement uncertainty. The overall or combined uncertainty originates from random and systematic errors.

Practical ways of estimating the measurement uncertainty are provided by the use of series of results obtained either by the analysis of certified reference materials (CRM) or from the participation in proficiency tests.

Both approaches were used to estimate the uncertainties associated to the determination of mass fractions of major and minor elements in silicate rocks by X-ray fluorescence spectrometry (XRF). Thirty test portions of CRM BRP-1 (Basalt Ribeirão Preto) were prepared as glass disks and analysed according a routine procedure. The results were used to calculate the relative standard uncertainty, the relative measurement bias and the standard deviation of the mean. The uncertainties of the reference values were also taken in account to obtain the expanded combined uncertainty (U%), approximating the 95% confidence level.

In the second approach results from ten rounds of the Proficiency Test Geo*PT*ä run by the International Association of Geoanalysts (IAG) were used to calculate the uncertainty associated to trueness. This approach covers a wider range of mass fractions.

Table 1 presents the estimated U% values. The last line shows the expected reproducibility among laboratories for BRP-1, calculated by the modified Horwitz expression. Overall, the uncertainties calculated using the proficiency tests results are higher than those obtained by the analysis of the CRM, except for MnO_2. Such higher U% values arose from bias, since the same values of within laboratory reproducibility were used to calculate both combined uncertainties. The data indicate that realistic mean values of uncertainties associated to routine measurements would better estimated analyzing several CRM to cover the mass fractions of interest.

Table 1. Expanded uncertainties obtained using thirty analytical results of a CRM and ten of proficiency tests compared to the calculated reproducibility among laboratories.

U (%) uncertainty	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
CRM BRP-1	1.2	1.6	1.9	2.4	7.9	2.2	1.8	3.8	3.7	2.1
Proficiency test	1.5	4.2	2.7	3.0	5.5	3.8	3.4	4.3	5.0	7.3
$2\cdot(Hc = 0.01\cdot c^{0.8495})$	2.2	3.3	2.7	2.6	5.1	3.2	2.9	3.4	3.8	4.3

PT.68

Comparision of data with field and laboratory methods

Hilda RS[1], Estela CJ[1], Ana BT[1]
[1]Universidad Nacional Autonoma de Mexico - Laboratorio de suelos y agua

Four variables of water quality (pH, hardness, alkalinity and turbidity) were measured up in 85 water samples taken from different sites, directly in field with portable easy-use equipment, as well as in laboratory by normalized methods under the Mexican Norm. The purpose was validate the field measurements and to know if both techniques could throw significantly different data. A "t" test of contrast was done to compare paired information, with a confidence level of 95 %. Significant differences between techniques were not obtained for the variables of alkalinity and turbidity. On the other hand, measurements of pH showed the highest significant differences between both techniques because the precision of each one was really very different. The hardness showed significant differences but their origin was not located yet.

PT.69

Homogeneity Tests for a Rotary Sample Divider

Webber E[1]
[1]Geoscience Australia

Two rock types, a coarse-grained granite and a finer-grained volcanic rock, were used to test a Rotary Sample Divider attached to a Rocklabs Boyd Crusher for homogeneity. Approximately 3 kg of each rock type were broken down by a jaw crusher, and then processed through a Boyd Crusher with splits taken using the attached rotary sample divider. The formula 10/(100-(10*n)) — where n is the number of the split — was used to process the entire sample, i.e., 10% of the first split was taken and remainder returned to the Boyd crusher; 11% of the second split taken and remainder returned to the crusher; 12.5% of the 3rd one taken and remainder returned to the Boyd crusher etc., until all the sample was used and there were 10 roughly equal splits. Each split was halved and each half pulverised for 3 minutes in a tungsten carbide ring mill for 3 minutes. Pressed powder pellets and lithium borate glasses were made and analysed using a PW2404 XRF spectrometer. The results of major and trace element analysis show that there is no apparent bias between either individual splits or from the first split to the last split, indicating homogeneity was achieved using the rotary sample divider.

PT.70

Tracing the La Plata River impacts on the depositional processes at the S/SE Brazilian continental shelf during the Holocene.

Nagai RH[1], FIGUEIRA RCL[1], Sousa SHM[1], Rodrigues I[1], Benites M[1], SILVA CEA[2], SALAROLI AB[1], Mahiques MM[1]
[1]IOUSP, [2]IQUSP

The La Plata River basin is the second largest drainage basin in South America, and its discharge to the western South Atlantic is strongly influenced by the South American Monsoon System. The northward penetration of shelf waters related to the La Plata River discharge impacts modern depositional processes in the S/SE Brazilian shelf. Marine sedimentary records provide important information for paleoceanographic and paleoclimatic reconstructions. Thus, the main goal of this study is to reconstruct the paleoenvironmental changes that occurred in the southern Brazilian shelf during the last 7000 years by applying sedimentological (grain size) and geochemical (bulk sediment elemental ratios, total organic carbon content and organic matter $\delta^{13}C$) proxies in two marine sedimentary records and its relationship with the paleoclimatic changes that took place in SE South America. Grain size and geochemical data highlight the occurrence of important changes in the depositional processes on the southern Brazilian shelf, probably related to changes in the source of sediments. From 2000 cal years B.P. towards the Present significant increases in the mud contents and in the Fe/Ca and Ti/Ca ratios, point to a progressively higher influence of the Plata Plume Water in the shelf system. This is consistent with a scenario of relatively more humid conditions in southeastern South America due to the southward displacement of the Intertropical Convergence Zone and the intensification of the South American Monsoon System that took place throughout the Mid to the Late Holocene.

PT.71

Chemical analyses of the Quaternary fluvial terraces at Careiro-Castanho and Autazes, central Amazonia

Soares EAA[1], Hazenfratz R[2], Verceze RC[2], Munita CS[2], Gonçalves ES[1]
[1]Universidade Federal do Amazonas, UFAM, [2]Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP

Three quaternary fluvial plains, formed by the Solimões and Amazonas Rivers, are present in the region of Careiro-Castanho and Autazes, south of the city of Manaus, Central Amazonia. They are divided in upper (TS), intermediate (TI) and lower terrace (TInf). Their distribution is asymmetric, covering the cretaceous Alter do Chão Formation in continuous stripes of more than 100 kilometers in length, with the long axis in the NE-SW direction. The vertical extent ranges from 23 to 70 meters above sea level. Granulometry of the sediments ranges from sands (quartz, feldspar and micas) to mud (silt and clay minerals) in different proportions, forming inclined heterolithic stratification (IHS) in point bars. Despite being inactive in the present, TS has the largest distribution in the studied area, and is only partially covered by water during the annual floods. It has therefore undergone some erosion, forming low hills, covered by intermediate to high vegetation. The sediments, red in color, present moderate to intense pedogenetic features, with intercalated soil horizons. The TI and TInf terraces are completely covered by water during the floods, thus being very plane, and only low vegetation is present. The color of the sediments is usually gray, partially due to high organic matter content, and pedogenesis is incipient. The presence of IHS in point bars in the asymmetric fluvial terraces indicate that both the Amazon and Solimões were meandering rivers during the Pleistocene, with a general northward migration tendency. The intrinsic lateral mobility of the river channel led to deposition, abandoning and exposure of the TS deposits during the last 100.000 years. For the present work, 50 samples from the three terraces were analyzed using instrumental neutron activation, to determine the concentrations of Na, As, Fe, Ce, K, Sc, Cr, Hf, Cs, Sm and U. The results were interpreted using forward stepwise discriminant analysis, distinguishing two sample groups. Chemical and mineralogical transformation of the TS deposits show more weathering influence when compared to TI and TInf.

PT.72

Determination of Trace Titanium Contents in Peridotites by X-Ray Fluorescence Method

Tatiana Aisueva, Marina Gornova
Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Irkutsk, Russia
* Presenting author: e-mail: aisu@igc.irk.ru

The titanium is incompatible element in the system peridotite-melt and as a result its content decreases regularly to a few ppm with increasing degree of mantle substrate melting. Content of titanium also depends on the mechanism of fusion and composition of melting substrate. Therefore, determination of trace titanium concentrations in the peridotites is important for the reconstruction of magmatic rocks genesis. Currently, there are few methods to solving this geochemical task. One such method is inductively coupled plasma mass spectrometry (ICP-MS). However, ICP-MS is expensive and time-consuming method, in this connection, the alternative express method is required. The nondestructive X-ray fluorescence analysis (XRF) is perspective for these investigations.

The results of the determination of trace titanium contents in the peridotites by XRF are presented in this paper. The measurements were performed using X-ray spectrometer S4 Pioneer (Bruker AXS), equipped with Rh target X-ray tube. Conditions of measurements are: the accelerating voltage of 50 kV, current of 40 mA, crystal analyzer LiF200, collimator with an angular resolution of 0,23˚, flow proportional detector. Samples were prepared as pressed pellet on the substrate from boric acid. The national reference certified materials (CRMs) of rocks, also Japanese and United States CRMs of rocks were used for calibration and assessment of analytical accuracy. The lack of CRMs with titanium content below 100 ppm is one of the problem in the titanium determination by XRF. Artificial mixtures were prepared for this range of contents. The titanium concentrations were calculated applying the software SPECTRAplus. The dependence of determination of trace titanium content on the type of calibration function was studied. The detection limit (3s) is 1 ppm.

Comparison of XRF results with data of ICP-MS was performed. The difference in results between two methods, in the range of concentrations from 10 to 100 ppm, was 15%. The results obtained based on the two different methods allow to improve the reliability of determination of trace titanium content in peridotites, and possibly to detect errors in analysis.

PT.73

Geothermometry on spring waters from Poços de Caldas, Minas Gerais, Brazil

Ritter S.M.[1], Isenbeck-Schröter M.[1], Bonotto D.M.[2]
[1]Universtity of Heidelberg, Institute of Geosciences, [2]Universidade Estadual Paulista Campus de Rio Claro - Instituto de Geociências e Ciências Exatas

Chemical Geothermometers were applied to spring waters from the city of Poços de Caldas in order to estimate maximum reservoir-temperatures and infiltration depths of meteoric water in the geothermal system. Five natural discharging thermal and non-thermal springs were analyzed with respect to major cation and anion contents. The five spring waters could be divided into two groups. Considering their chemical evolution adds up to a classification of non-thermal dilute weakly acidic shallow groundwaters and thermal alkaline waters of deeper origin, which are more mineralized. One sample gives reason to be a mixture of both groups. The thermal waters have a specific chemical composition, which reflects the extraordinary geological setting of the geothermal system and its mineralogical features of the Poços de Caldas alkaline complex with prevailing phonolites and nepheline-syenites. The thermal waters are characterized as alkali-hydrogen carbonate waters with elevated concentrations of sulfate and fluoride. An intensively discussed evolution of the geothermal fluid including geochemical modeling using an inverse approach on predominant rock-water interactions leads to the negation of *silica*-Geothermometer application at Poços de Caldas spring waters. It is suggested that all earlier subsurface-temperature estimations on the basis of temperature dependent quartz-dissolution-equilibrium have to be reconsidered, hence feldspathoit-bearing rocks prohibit the occurrence of quartz as a pure phase in their mineral paragenesis. In spite of this fact, the high dissolved silica measured concentrations are most likely caused by silicate weathering. *Na/K*-Geothermometers are more suitable for Geothermometrics on the waters, as the system can be assumed to have reached chemical equilibrium. Subsurface-temperature estimations calculated with the computer tool *SolGeo* indicate maximum equilibrium temperatures of the spring waters reservoir of 105-130 °C for several *Na/K*-Geothermometers. This offers estimates on reservoir-depth of 2.6-3.3 km, regarding a median geothermal gradient of 32.5 °C/km and an annual mean temperature of 19 °C at the Poços de Caldas plateau.

PT.74

Drift correction to ensure long term stability of X-ray fluorescence spectrometer results

Loubser M[1]
[1]PPC Cement - Group Quality Sevices

Accurate and precise XRF analysis is crucial when a production process is monitored using mainly this technique. In a high throughput analytical environment it is very difficult to schedule instrument time to recalibrate regularly so it is of utmost importance to have good drift correction systems to ensure long term stability. Most instrumental software packages include drift correction software to ensure long term stability and modules like Statistical Process Control (SPC) to monitor this.

Problems arise when the software algorithms fail and either do not correct for drift effectively, typically due to over or under correction.

In this paper a case study will be described where a drift correction system was evaluated on seven different spectrometers of different age and models, but with similar software. The standard drift correction algorithm, with a set of drift monitor samples were found to be very effective for long term stability as long as the actual instrument drift remained within certain limits. When drift became excessive; due to X-ray tube failing or instrument aging, the algorithms and monitors were unable to ensure comparable results. Different approaches to rectify this will be described in this paper.

PT.75

Production of an iron formation quality control reference material

Sampaio GMS[1,2], Enzweiler J[2], Nalini Jr HAN[1], Navarro MS[2]
[1]Universidade Federal de Ouro Preto - DEGEO/UFOP, [2]Universidade Estadual de Campinas - IG/UNICAMP

Reference materials for quality control (QCM) can be valuable to establish the metrological traceability of measurement procedures. Such materials represent routine samples and must be stable and sufficiently homogeneous for the intended use. Very few reference materials of iron formation (IF) matrix are available and their trace element mass fractions are poorly known. Compared to other geological matrices, IF have typical low content in rare earth elements (REE). These elements are of great interest to study ancient geological processes and the chemical composition of the oceans at the time of their deposition.

Few published methods and data related to the determination of REE in IF are available. The absence of reference materials (RM) with certified values for REE hinder proper validation of the analytical procedures, which must include complete sample dissolution. Acid dissolution procedures, without and with pressure, were applied to measure 28 trace elements in five IF reference materials and three unknown samples by inductively coupled plasma mass spectrometry equipped with collision cell. The results obtained for the RM FER-1, FER-2, FER-3, FER-4 and IF-G were compared to published data. The addition of water to the acids before applying pressurized decomposition resulted in consistently higher values for heavy REE in some of the analyzed RM. One QCM was prepared from a sample of friable Itabirito, from Quadrilátero Ferrífero (MG), chosen among the unknowns. About 6,5 kg from the sample was pulverized using an agate grinding jar and a vibratory mill. After homogenization, the material was divided resulting in 64 bottles of 100 g each. Ten bottles were randomly selected and two test portions of each were digested using acid decomposition with pressure and analyzed under repeatability conditions for the study of homogeneity. The QCM showed to be sufficient homogeneous, i.e. the compositional variance between bottles is statistically insignificant compared to the analytical variance, and suitable for the intended use. The relative standard deviations of characterization for the REE were between 1.7 and 5.8 %. Due to the absence of an iron formation CRM, the basalt BRP-1 was analyzed to ensure the metrological traceability to the produced QCM results.

PT.76

The Youden plot as a tool for the evaluation of interlaboratory comparison studies aiming the certification of reference material

Moreira EG[1], Vasconcelos MBA[1], Maihara VA[1], Catharino MGM[1], Saiki M[1]
[1]Instituto de Pesquisas Energéticas e Nucleares - Centro do Reator de Pesquisas

The Youden plot is a graphical means to evaluate interlaboratory comparison results and it is used when each participant laboratory presents two results for the same sample or results for two different samples. It is a simple but effective method for comparing the variability between laboratories, but also within each laboratory. With its aid, it is possible to check if there are repeatability problems within laboratories (within-laboratory variation) and if there are laboratories whose results are considered extreme and therefore likely to be eliminated in the study (between-laboratory variation). The Youden plot may be used as a preliminary tool in projects aiming the certification of new reference materials. This study presents the application of Youden plots to the results of an interlaboratory comparison designed for the characterization of the mass fraction of 36 elements in a mussel reference material produced in Brazil. This reference material was planned as a quality assurance tool for element biomonitoring studies along the Brazilian seashore. Element mass fractions were determined by seventeen laboratories and the following analytical techniques were applied: Neutron Activation Analysis (NAA), Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-Ray Fluorescence (XRF), and Alpha Spectrometry (α-ESP).

PT.77

Assessment of an interference on selenium measurement in the analysis of mineral waters by ICP-OES

SOUZA, C.F.[1]*; BARANDAS, A.P.M.G.[1]; MAXIMIANO, D.H.S.[1]; TEIXEIRA, E.M.G.P.[1]; GOUVEA, G.P.M.[1]; DUARTE, M.A.I.[1]
[1] - CPRM – Serviço Geológico do Brasil
* cabrini.souza@cprm.gov.br

The Mineral Analysis Laboratory (LAMIN) / Geological Survey of Brazil (CPRM / SGB) employs ICP-OES analysis to determine dissolved metals in mineral water. To comply with Brazilian standards for health related limits for certain substances 28 elements, including selenium, are determined in mineral water. Brazilian regulations (MS No. 2914 and RDC 274 ANVISA), establish the maximum allowed limit for selenium as 10 µg L^{-1} so the analytical method should be able to quantify selenium below this limit. An analytical procedure based on the method SM 3120 from SWEWW 21st ed. was tested in our laboratory to analyze this element. The quantification limit was estimated by external standard procedure. Standard solutions were analyzed in the range of 5 to 25 µg L^{-1} with good linearity (correlation coefficient greater than 0,998). The first point of the curve being the quantification limit. Reference material SRM 1643e was used to verify the accuracy of the method for various metals including selenium. The analytical recovery for selenium in this SRM was satisfactory (between 90 and 110%). However, when mineral water samples, of different compositions, were spiked with selenium the recovery for this element was no greater than 60% evidencing a matrix effect for selenium in mineral waters. Reference methods SM3120 and EPA 200.7 indicate iron as the main interferent for selenium. However analysis of selenium in SRM 1643e, which contains iron (98.1 ± 1.4 mg L^{-1}), did not show any interference as stated above. The composition of SRM 1643e was then compared with the elemental composition usually found in Brazilian mineral waters. Silica, as SiO_4, is always present in mineral water, but is absent in SRM 1643e and could therefore be the interferent. Reagent water spiked with known amounts of selenium and silicon were then prepared and only 60% recovery was found for selenium. Both reference methods were then ruled out for the analysis of selenium by ICP-OES in mineral waters. Different sample pretreatments, introduction methods or hyphenation of the ICP-OES with hydride generation, have to be considered to overcome the matrix effect for selenium evidenced in mineral waters.

PT.78

Analytical methods for geochemical mapping using meliponídea honey (Tetragonisca angustula)

Oliveira F A de[1], Nascimento N de O[2], Abreu A T de[1], Antonini YI[3], Nalini Júnior H A[1]
[1]UFOP - Universidade Federal de Ouro Preto - DEGEO - Departamento de Geologia, [2]UFOP - Universidade Federal de Ouro Preto - DEBIO - Departamento de Biodiversidade Evolução e Meio Ambiente, [3]UFOP - Universidade Federal de Ouro Preto - DEBIO - Departamento de Biodiversidade

Honey is a versatile bioindicator and has been used to obtain elemental distribution maps. The determination of elements in honey is a challenging task. This study evaluated two methods of acid digestion: in PTFE vials (Savillex®), heating maintained at 90 °C on a hotplate for a period of approximately 30 hours, and using the microwave for 35 minutes at 200 °C, with an output of 1000 Watt. Samples of *Tetragonisca angustula* honey were digested in 7.0 mL of 65% HNO3 (Merck, PA, ACS, ISO) and 1.0 mL 30% H2O2 (Merck, ISO). The reagents were added gradually to the samples digested in the PTFE vials (Savillex®). The analyses were performed in triplicate. The digested samples were transferred and Milli-Q® ultrapure water was added to a final volume of 50 mL.

The elemental concentrations in the extracts were measured by inductively coupled plasma optical emission spectrometry (ICP OES) (Spectro Ciros CCD) and inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700x). The results obtained by both acid digestion methods and techniques were compared for some elements. The following elements were determined by ICP-MS: Mg, Al, V, Cr, Mn, Zn, Sr, Ba, and Cd, and by ICP OES: Al, Ba, Ca, Cu, Fe, K, Li, Mg, Mn, Na, P, S, Si, Sr and Zn. The metal concentrations measured by ICP OES after acid digestion using microwave were higher than those measured using hotplate heating. This effect was observed for Al and Si and also for Cr measured by ICP-MS. The elemental concentrations in the extracts measured by ICP-MS and ICP OES were statistically different, except for Mg. Further studies should follow in order to evaluate the matrix interferences, by using the internal standard, calibration by standard addition, matrix separation and correction with mathematical models.

PT.79

Using Simplex Algorithm for Exact Multielement Matrix-Matching applied to the characterization of Limestone CRMs by Induced Coupled Plasma Spectrometry

Zucchini, R.R. and Hama, P.
Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A. - Laboratório de Referências Metrológicas

In spectrometry, matrix effects due to differences between chemical compositions of calibration standard solutions and samples usually produce analytical bias. Matrix matching is a calibration strategy that can be used in order to reduce these effects and improve the accuracy of the results. In general it can be said that the closer the matching the smaller the bias. Using calibration solutions with exact sample matrix matching, in theory, can remove almost completely these matrix effects. Despite of this, exact matching, particularly in multi-element calibration, is not extensively reported, perhaps because of peculiarities that make calculations quite laborious. This paper presents an application of the classical linear programming simplex algorithm for numerically solving the problem of preparation of a set of multi-element calibration standards with exact sample matrix matching, employed in the chemical characterization of some limestone certified reference materials.

PT.80

Ceramic humidity sensors for tropical forests monitoring

Oliveira, R. M.[1] e Nono, M. C. A.[1]
[1]Grupo de Pesquisa em Tecnologias Ambientais – TECAMB
Laboratório Associado de Sensores e Materiais – LAS
Instituto Nacional de Pesquisas e Materiais – INPE, São José dos Campos, SP - Brasil
Avenida dos Astronautas, 1758, Caixa Postal: 515 - 12.1201 - 970
E-mail: rodmatos@las.inpe.br

Many types of sensors for eenvironmental monitoring are commercially available, but they do not satisfactorily meet the specific needs of the country, because they are designed for different conditions. In the monitoring of environmental parameters, the climatic differences in Brazil should be considered, which make necessary the development of sensors for each region of the country. Thus, researchers of the Environmental Technologies Group (TECAMB) integrated to the Associate Laboratory of Sensors and Materials (LAS) of the National Institute of Space Research (INPE) have been involved for the past 20 years, in the elaboration of diagnosis techniques, characterization and development of porous ceramic. In this work, porous ceramic was manufactured by mechanical mixture of ZrO_2 and TiO_2 powders, compacted and sintered at different temperatures, for application as air humidity sensing elements in the Project "Development and Application of Network of Geosensors for Environmental Monitoring", into a co-operation programme under the Microsoft Research-FAPESP Virtual Institute for IT Research, for tropical forests monitoring. Ceramic materials applied as sensing elements of humidity, specifically metallic oxides, have shown advantages in terms of their mechanical strength, their resistance to chemical attack and their thermal and physical stability in, mainly, hostile environments. It is noteworthy that the ceramics exhibit a unique structure, consisting of grains, grain boundaries, surfaces and pores, what make them appropriate to be used as humidity sensors, since they have controlled microstructures and suitable chemical compositions. The characterization of the sintered ceramics were carried out through measurements of B.E.T. (specific area of porous), nitrogen and mercury porosimetry (pore sizes distribution), scanning electron microscopy SEM (microstructure) and X-ray diffraction (crystalline phases). The density was determined by Archimedes method. The porous ceramic characterization as relative humidity sensor element was accomplished through capacitance measurements using a RLC bridge in climatic chamber. The results evidenced that the air humidity ceramic sensing elements are very promising ones.

PT.81

The Vitoria-Trindade Ridge and its Islands – Trindade & Martin Vaz – Lithogeochemistry analysis

Anderson Costa[1]; Mauro Cesar Geraldes[1]; Thaís Vargas[1];
[1]UERJ, E-mail: andcostasantos@gmail.com; geraldes@uerj.br; taisvargasuerj@gmail.com;

The Vitoria-Trindade Ridge comprises islands, seamounts and guyots found along parallel 20°30'S for more than 1.200 km. VanDecar *et al.,* (1995) suggest that this ridge is not related with plume but only to magmatism resulting from weak transform faults. Fodor & Hanan (2000), suggest the existence of magmatim generated by hotspot according to geochemical evidence based on ankaramitic Columbia seamount about 10 Ma (Gripp & Gordon, 1990). Without going into this question, it is known that the above mentioned islands occur in 70 Ma oceanic crust (Parsons & McKenzie, 1978). Trindade island is found 600 m above sea level; Martin Vaz, 175 m and seamounts and guyots, 4-5 km from the ocean floor not emerging. Dredging in the seamounts was performed by the Brazilian Navy in March 2011 and systematic field work was carried out in February 2011 on the islands. Geochemical analyses of whole rock for major and trace elements were obtained by alkaline fusion ICP-OES and ICP-MS methods. Seven samples of Trindade & Martin Vaz islands and one sample of seamounts were purposely duplicated and results showed differences of less than 0.65% between themselves. The good method reliability allowed the use of the data for proper lithogeochemistry interpretation.

PT.82

Standardless analysis of limited amounts of aluminum silicate materials by WDXRF

PAZ SPA[1], Angelica RS[2], Menezes RA[2], Silva RAM[3]
[1]UNIVERSIDADE FEDERAL DO PARA - FACULDADE DE ENGENHARIA DE MATERIAIS, [2]Universidade Federal do Pará - Instituto de Geociências, [3]Universidade Federal do Pará - Faculdade de Engenharia Química

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Zeolites and other porous materials have been synthesized from kaolin via metakaolin since a long time. New synthesis routes nowadays are using very small amounts of reagents and consequently small amounts of the synthesized products are formed representing a challenge for quantitative chemical analysis by WDXRF that use traditional sample preparation procedures (several grams) for fused beads and pressed powders. In this work, orientation surveys were carried out with small amounts of kaolin and zeolite samples ranging from 0.1 to 3.0 g. The following major elements have been analyzed: SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 (standardless analysis) in a thin layer of sample pressed onto a boric acid backing. The reference material for the validation tests was a Kaolin sample (KGa-2) from the source Clays Repository of The Clay Minerals Society. The quality assurance evaluation of the results was based on standard deviation (SD) and standard error (SE) values and showed that up to 0.5 g of sample was possible to obtain acceptable values for a semiquantitative analysis, which to some extent already fulfills the chemical control of the materials produced in this type of activity, i.e., meets this level of control. SD and SE values for the analyzed elements are as follow: SiO_2 (0.15 and 1.83%), Al_2O_3 (0.13 and 1.3%), Fe_2O_3 (0.08 and 0.2%) and TiO_2 (0.11 and 0.15 %) (sample preparation with 0.5 g sample). After this validation phase of the method, further analysis of the synthesized products (zeolites) and the kaolin from the Amazon region used for the synthesis (starting material) are still in progress.

PT.83

Soil stabilization and the quality control of engineering properties modification of Nile Delta silty clay soil to be applicable as road bases

Ismail, A. I. M.[1] and Ryden, N[2]
[1]Geological Sciences Dept., National Research Centre, Egypt
ali_ismail_2000@yahoo.com
2 Dept. of Engineering Geology, Lund Institute of Technology, Lund, Sweden

Clay soil with low bearing capacities can present great problems underlying pavement and light structures due to uncertainty associated with their performance. They are often unstable and structure and they are susceptible to problems from changes in moisture content. It is possible to overcome the problems by strengthening the soil underlying the structure or diminishing the leads transmitted from the foundation to the soil. Clay soils tend to swell and become soft when wetted and may shrink and become stiff when dried. From an engineering aspect, an increase in water content has a number of disadvantageous consequences: cohesion decreases, the soil swells, the alternating dry-out/shrinkage and wetting/swelling effects destroy the rock or soil structure.
These precautions can be taken by modifying the foundation system and /or altering the soil itself or improving the properties of the soils, which can be achieved either by chemical stabilization. From a construction point clayey soil materials are unfavourable to building ground due to the change in water content. To achieve a satisfactory foundation, the clay rich materials and the medium to highly plastic soils have to be exchanged by sand and gravel or sufficiently improved. The improvement of the soil materials could make the material suitable as fill materials, foundation and / or road base construction for dam sections. The quality control for the stabilized soils was investigated using sonic measurements and strength gain.

PT.84

Construction and Automation of ^{137}Cs Vulnerability Maps of Soils

Wasserman MAV[1], Picanço Jr P[2], Ribeiro JA[2], Wasserman JC[3]
[1]Instituto de Engenharia Nuclear - SETER, [2]Universidade do Estado do Rio de Janeiro - Faculdade de Engenharia, [3]Universidade Federal Fluminense - Rede UFF de Meio Ambiente e Desenvolvimento Sustentável

The radioactive contamination of agricultural systems generally derive from the nuclear industry that can be routinely or accidentally released into the atmosphere, followed by dry or wet deposition on soil, biota and superficial aquatic systems. Previous radioecological studies have shown that soils with low pH, low organic matter content and low fertility are more vulnerable to contamination by ^{137}Cs, since the mobility of the radionuclide between soil and plants compartments is high. This study developed a methodological tool to map soils according to their vulnerability to ^{137}Cs contamination, based on soil chemical properties. For this, a conceptual model based on reference values of the transfer factor soil-plant (TF) for ^{137}Cs in cereals was created, relating soil variables (pH, CEC and exchangeable K), relevance of parameters and amplitudes of variations to each TF value range. The vulnerability of ^{137}Cs contaminated soil was defined considering four categories: 1) extreme vulnerability, TF ≥ 1 and remain elevated for several years after soil contamination; 2) high vulnerability; 1 ≥ TF > 0.1 and; 3) moderate vulnerability, 0.1 <TF ≥ 0.01; 4) low vulnerability, TF < 0.01 and diminish with the aging of soil contamination. After the definition of vulnerability categories, the automated process of classification has been tested and equalized on a conceptual test area composed by Brazilian soils, with known soil properties, but with unknown TF, and others soils from tropical, subtropical and temperate areas, whose TF values for ^{137}Cs and soil properties were available in scientific literature. The classification of vulnerability that was obtained from the automation of the conceptual model, validating the predicted data in relation to other published studies. After validation, the process was applied to soils from Castro, Paraná, Brazil. The soils from that region presented a moderate level of vulnerability to ^{137}Cs contamination and the expected TF in those soils was < 0.1 and ≥ 0.01. This result was very close to previous studies in Nitisol, also located in a subtropical area of Brazil, from which the TF for ^{137}Cs determined for cereals was 0.03. This automated model and also the mapping derived from vulnerability classification showed adequate to optimize the actions of emergency planning in rural areas, since it allows the prediction of the value of TF which is essential for radioecological risk assessment and it also helps to identify the most vulnerable areas and the most appropriate remediation measurements for the site, in case of accident.

PT.85

Mercury distribution in sediments of the Juturnaíba dam, Rio de Janeiro, Brazil

Souza, VA[1], Wasserman, J.C.[2]
[1]Universidade Federal Fluminense - Dept. de Geoquímica, [2]Universidade Federal Fluminense - REMADS-UFF

Mercury is a toxic element that is widely distributed in contaminated as well as remote environments. However, the release of this pollutant from anthropogenic activities and its long range atmospheric transport have significantly increased its concentrations in the aquatic environment and consequently in the biota. In the case of the Juturnaíba lake, part of the landscape was flooded after the construction of a dam, favoring the development of anoxic conditions, reducing the redox potential within the sediments and modifying the geochemical conditions. The understanding of the pollutants behavior in the Juturnaíba is necessary, because the system is a multi-purpose environment that is used for water supply, agricultural irrigation, leisure and fishing. In the present study, we evaluated the mercury contamination of the sediments of the Juturnaíba dam in order to determine whether this pollutant may constitute an environmental threat to humans. 32 surface sediment samples were collected in April 2011 in order to carry out the total mercury analyses by cold vapor atomic absorption spectrometry (CV-AAS). The relationship between total mercury concentrations and total organic carbon and granulometry allowed further interpretations of the results. The distribution map indicates that the highest mercury values (211 ng g^{-1}) occur associated with the presence of aquatic macrophytes banks. In the central portion of the lake, some relatively high values were also observed (209 ng g^{-1}) that may be associated with the effluents of two water treatment plants present in the area. The lowest values (58 ng g^{-1}) were observed in the Southern portion, associated with the inputs of the São João River that drains a better preserved area. It looks like that the main sources of mercury in the region are associated with domestic sewages and very small industries that are present in the region. Some contribution from agriculture and cattle may also be present. It is necessary to underline that the highest concentrations occur in an area of significant macrophyte production, where methylation process may be more significant, constituting a threat for humans and the environment.

PT.86

Assessment of trace metals mobility in sediments from Admiralty Bay, Antarctica, using a sequential extraction procedure

Ribeiro AP[1,2], Demane G[2], Tramonte KM[1], Batista MF[1], Pereira AM[1], Silva CRA[1], Ferreira PAL[1], Figueira RCL[1]
[1]Instituto Oceanográfico - Universidade de São Paulo, [2]Universidade Nove de Julho

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The three-stage sequential extraction method, known as BCR procedure, based on Standards, Measurements and Testing Programme of the European Community Bureau of Reference, was used to determine the mobile fractions of Cu, Ni, Pb and Zn in sediments collected from different sites (Ferraz Station, Botany Point, Ullman Point and Refugio) in the Admiralty Bay, during the 28th Brazilian Antarctic Expedition in the 2009/2010 Austral summer. The quality of data was found to be satisfactory from the analysis of the certified reference material BCR-701. The recovery values for Cu, Ni, Pb and Zn ranged between 93-113%, 109-113%, 93-111% and 90-115%, respectively. Zn and Ni were mainly found in the residual fraction, reflecting their natural contribution in the Admiralty Bay. Cu and Pb exhibited high potential mobility, above 70% for most of the sediment samples analyzed. Notwithstanding, Pb contents ranged from 4.1 to 7.8 mg kg^{-1}, i.e., Pb concentrations were well below the Threshold Effect Level value, according to the Canadian Environmental Guidelines. Cu presented higher levels, reaching 75 mg kg^{-1} in Ferraz Station. These values are above the Canadian Probable Effect Level, indicating that adverse biological effects to aquatic organisms should be observed. Nevertheless, since the disturbances are seldom observed in Admiralty Bay, according to the data set, Cu is preferably bound to organic matter.

PT.87

Determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in wild mushrooms and soils collected in Poços de Caldas region

Rosa M.M.L.[1], Maihara VA[2], Taddei M.H.T.[1]
[1]Comissão Nacional de Energia Nuclear - Laboratório de Poços de Caldas - LAPOC, [2]Instituto de Pesquisas Energéticas e Nucleares - Centro de Reator de Pesquisa

Studies have shown that wild mushrooms from different regions can be used as indicators of environmental contamination and ecosystem quality. The radionuclide transfer from soil to organic matter determines the extent of radioactive contamination around the nuclear facility. This, consequently, can constitute a risk of public exposure to radioactivity from the ingestion of food. The objective of this study was to determine radionuclides such as ^{226}Ra, ^{228}Ra, ^{210}Pb in samples of wild mushrooms and soils collected from the region of Poços de Caldas Plateau. This area is of great interest, because it presents high natural radioactivity and there was the first Brazilian uranium mine. Seventy areas of radioactive anomalies have been identified in this region. Twenty-four mushroom and soil samples were collected in humid areas under trees or in open fields from seven points, being two of them close to the high radioactive anomalies regions. For the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in mushroom samples a radiochemical separation followed by alfa and beta spectrometry was employed. These same radionuclides were determined by gamma spectrometry in soil samples. For validation of both methodologies soil IAEA 327 reference material was analyzed. Chemical yields for Ra isotopes were in the 73 to 99% range and 61 to 84% for Pb. The ^{226}Ra, ^{228}Ra and ^{210}Pb activity concentrations ranged from 1.0 to 170 Bq kg^{-1}, 0.6 to 120 Bq kg^{-1} and 6 to 230 Bq kg^{-1} for wild mushrooms, respectively. For the soil samples the ^{226}Ra, ^{228}Ra and ^{210}Pb activity concentrations ranged from 68 to 270 Bq kg^{-1}, 29 to 255 Bq kg^{-1} and 52 to 392 Bq kg^{-1}, respectively. The result showed a variation of radionuclide activity in different areas of the region. Most samples showed higher Ra isotope activity when compared to ^{210}Pb. This is probably due to ^{210}Pb transfer in the environment especially through fallout, whereas Ra is essentially transferred by solution through bodies of water.

PT.88

Potential availability of chromium in soils under the influence of different industrial activities

Jovana Bavaresco[1], Maria Lucia Kolowski Rodrigues[2] e Clésio Gianello[1]
[1-] Universidade Federal do Rio Grande do Sul – Departamento de Solos
[2-] Fundação Estadual de Proteção Ambiental Henrique Luís Roessler (FEPAM-RS)

In environmental studies it is often accepted that soils consist of different geochemical phases, in a variety of structural forms that act as metals reservoirs. When there is an interest in characterizing the potential availability of metals in contaminated soils, the study of their distribution in these phases is more useful than the analysis of the total content of the elements. The overload of metal contaminants introduced into the soil by industrial activities generally leads to more unstable associations and presents greater potential availability for biological incorporation. In this study we investigated the distribution of chromium in the geochemical phases of soils under the influence of different industrial activities, which are known for their potential of environmental contamination by this metal: treatment of wood with chromated copper arsenate, CCA (A), manufacture of chromium salts (B) and leather tanning (C). The association of chromium with the different soil phases (exchangeable and/or soluble in acid, reducible and oxidizable) was evaluated using the sequential extraction scheme of the European Community and validated by the analysis of the certified reference material BCR701. The chromium analyses were performed by inductively coupled plasma optical emission spectrometry, ICP/OES. In the three types of soil evaluated, a major change was observed in the geochemical distribution of chromium compared to the respective reference samples. These reference values were established by evaluating soil samples from adjacent sites that had not been influenced by the respective industrial plant. The greatest relative increase in the chromium content always occurred in the oxidizable phase, suggesting its preferential association with organic matter, in the less toxic trivalent form. However, Soil B stood out from the others due to the major relative increase in chromium concentration in all the geochemical phases, including the most labile fraction of the metal. Considering the geochemical distribution observed and the knowledge of Cr(VI) content in the samples evaluated (A = 2 mg kg^{-1}, B = 450 mg kg^{-1} and C < 1 mg kg^{-1}), soil B revealed more critical conditions, with a greater potential for the mobilization of chromium into the surrounding environment.

PT.89

Reactive transport of arsenic in a contaminated sandy aquifer in Germany

Maier M.[1], Isenbeck-Schröter M., Ritter S.M.
[1]University of Heidelberg - Institute of Geoscience, Germany

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In order to identify reaction behavior and transport mechanisms of arsenic in a contaminated sandy aquifer, comprehensive soil and groundwater sampling as well as laboratory tests were performed. To predict the ongoing development of the contaminant plume at the remediation site a numerical model was calculated.

Extensive groundwater sampling of monitoring wells and direct push probing showed that soil contamination is limited up to 17 m depth. In this area the dominating species on the soil matrix and the groundwater samples is As(V), below the As(III) fraction increases in groundwater samples and becomes the dominating arsenic species. In horizontal down gradient direction the ratio of As(V) to As(III) decreases. The observed species distribution can be related to the redox conditions in the aquifer, where suboxic milieu conditions tend to get anoxic with increasing depth. Under such redox conditions As(III) is the dominating species and due to higher mobility its vertical and lateral dispersion is wider than that of As(V).

Various column tests with more and less contaminated aquifer material were performed adjusting changing conditions from anoxic to oxic and vice versa. Rapid change of arsenic speciation distribution was investigated depending on the redox conditions. This process is reversible in all directions.

A numerical transport model using MODFLOW was set up and calibrated with field data. One scenario simulating a proceeding remediation stated the hydraulic stability of the contamination plume within the next decades. According to the model, stopping of remediation at any time will lead to contaminants arrival into drinking water extraction within some hundreds of years. This is a result of continuous leaching of contaminations in the contamination source in the unsaturated zone and the mobility characteristics of arsenic under anoxic conditions.

Further investigations are planned in order to optimize the ongoing remediation or to develop an efficient immobilization or removal technique.

PT.90

Studies of the FTIR response variation among different apatite crystals

Palissari R[1], Guedes S[1], Alencar I[1], Lixandrão Filho AL[1], Hadler JC[1]
[1]Universidade Estadual de Campinas - Instituto de Física Gleb Wataghin

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Apatite is the most widely used mineral in fission-track (FT) analysis [Tagami, T. and O´Sullivan, P. B., 2005, Rev. Mineral. Geochem., 58, 19-47]. The FT method is based on natural decay of uranium (^{238}U) that creates regions of damaged structure by passage of fission fragments. It is well known that the fission-track lengths are shortened by the combined action of time and temperature, which is called annealing. Geological thermal history modeled from apatite fission-track data requires knowledge of track annealing behavior and it has been shown that annealing is compositionally controlled. Fourier-transform infra-red (FTIR) reflected light microspectroscopy has been suggested as a fast non destructive way of characterizing apatite chemical structure in correlation with annealing kinetics [Siddall, R. and Hurford, A. J., 1998, Chem. Geol., 150, 181-190]. In this work, alkaline apatite crystals from Ponta Grossa and Alto Paranaíba Archs, Brazil, were analyzed with FTIR in order to find out if there are any observable variations in infrared peaks. In routine FT analyzes, grains are mounted in epoxy resin whose exact composition is unknown. It is shown that carrying out a subtraction of spectra (apatite/resin minus resin), after suitable renormalization, it is possible to obtain the separated apatite spectrum.

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